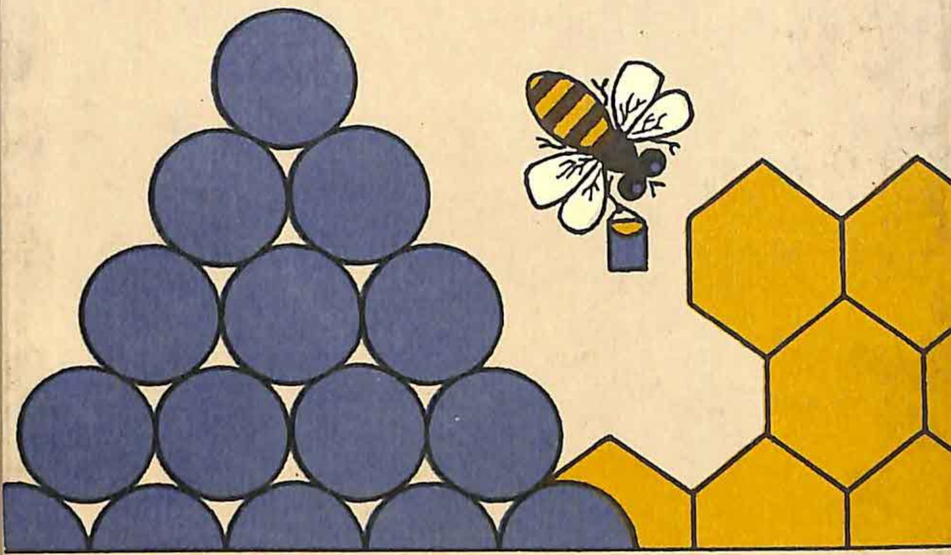
Book 2 Physics for Everyone

L. D. Landau, A. I. Kitaigorodsky



MOLECULES

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Physics for Everyone

Book 2

L. D. Landau
A. I. Kitaigorodsky

MOLECULES

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the Russian
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Mir Publishers Moscow

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PREFACE TO THE FOURTH RUSSIAN EDITION

This book has been named *Molecules*. Many chapters from the second half of a previous book, *Physics for Everyone*, by Lev Landau and Alexander Kitaigorodsky, have been included without revision.

The book is devoted mainly to a study of the structure of matter dealt with from various aspects. The atom, however, remains, for the time being, the indivisible particle conceived by Democritus of ancient Greece. Problems related to the motion of molecules are considered, of course, because they are the basis for our modern knowledge of thermal motion. Attention has been given, as well, to problems concerning phase transitions.

In the years since the preceding edition of *Physics for Everyone* was published, our information on the structure of molecules and their interaction has been considerably supplemented. Many discoveries have been made that bridge the gaps between the problems dealing with the molecular structure of substances and their properties. This has induced me to add a substantial amount of new material.

A long overdue measure, in my opinion, is the addition to standard textbooks of general information on molecules that are more complex than the molecules of oxygen, nitrogen and carbon dioxide. Up to the present time, the authors of most courses in physics have not considered it necessary to deal with more complicated combinations of atoms. But giant molecules have become extremely common in our everyday life in the form of a great diversity of synthetic materials. A new science, molecular biology, has been founded to explain the phenomena of living matter, using the language of protein molecules and nucleic acids.

Likewise undeservedly omitted, as a rule, are problems concerning chemical reactions. Such reactions belong, however, to the physical process of the collision of molecules, accompanying their rearrangement. It proves much simpler to explain the essence of nuclear reactions to a student or reader who is already acquainted with entirely similar behaviour of molecules.

It was found expedient in revising the book to transfer certain parts of the previous *Physics for Everyone* to the subsequent books of this series. It was considered feasible, for instance, to refer only briefly to sound in the chapter on molecular mechanics.

It was found advisable, in the same manner, to defer the discussion on the features of wave motion to the treatment of electromagnetic phenomena.

As a whole, the four books of the new edition of *Physics for Everyone* (*Physical Bodies*, *Molecules*, *Electrons*, and *Photons and Nuclei*) cover the fundamentals of physics.

April 1978

A. I. Kitaigorodsky

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1. Building Blocks of the Universe

Elements

What is the world surrounding us made of? The first answers to this question which have reached us originated in Ancient Greece more than 25 centuries ago.

At first glance, the answers seem as strange as can be, and we would have to waste a lot of paper in order to explain to the reader the logic of the ancient sages—Thales, having asserted that everything consists of water, Anaximander, having said that the world is made of air, or Heraclitus, in whose opinion everything consists of fire.

The incongruity of such explanations forced later Greek "lovers of wisdom" (that's how the word "philosopher" is translated) to increase the number of fundamental principles or, as they were called in antiquity, *elements*. Empedocles asserted that there are four elements: earth, water, air and fire. Aristotle contributed the final (for a very long time) corrections to this investigation.

According to Aristotle, all bodies consist of one and the same substance, but this substance can assume different qualities. There are four immaterial elements: cold, hot, moist and dry. Combining in pairs and being imparted to a substance, Aristotle's elements form the elements of Empedocles. Thus, a dry and cold substance yields earth; dry and hot, fire; moist and cold, water and, finally, moist and hot, air.

However, in view of the difficulty involved in answering many questions, ancient philosophers added a "divine quintessence" to the four elements. This was a kind of god-cook, cooking the various elements together. Of course, it isn't hard to explain away any perplexity by reference to a god.

But for a very long time—almost up to the 18th century—few dared be perplexed and ask questions. Aristotle's teachings were avowed by the Church, and any doubt in their validity was a heresy.

But these doubts arose anyway. They were engendered by alchemy.

In the distant past, into the heart of which we can look by reading ancient manuscripts, people knew that all bodies surrounding us were capable of being transformed into others. Combustion, sintering, the melting of metals—all these phenomena were well known.

This, it would seem, did not contradict Aristotle's teaching. The so-called "dosage" of the elements changed during any transformation. If the whole world consists of only four elements, the possibilities of transforming bodies should be very great. It is merely necessary to find the secret of what to do in order that any body might be obtained from any other one.

How tempting is the problem of making gold or finding a special, extraordinary "philosophers' stone", giving its possessor wealth, power and eternal youth. The science of manufacturing gold and a philosophers' stone, of transforming any body into any other one was called alchemy by the ancient Arabs.

The labour of people devoting themselves to the solution of this problem continued for centuries. Alchemists did not learn how to make gold, did not find a philosophers' stone, but made up for this by collecting many valuable facts about the transformation of bodies. In the final analysis, these facts served as the death sentence for alchemy. In the 17th century, it became obvious to many people that the number of basic substances—elements—is incomparably greater than four. Mercury, lead, sulphur, gold and antimony turned out to be undecomposable substances; one could no longer say that these substances were made out of elements. On the contrary, one had to rank them among the elements of the world.

In 1661 in England, Robert Boyle (1627-1691) published the book *The Sceptical Chemist*. Here we find a completely new definition of an element. This is no longer the elusive, mysterious immaterial element of alchemists. An element is now a substance, a component part of a body. This is consistent with the modern definition of the concept of an element.

Boyle's list of elements was not very large. He added fire to a correct list. Incidentally, the idea of elements lived on even after Boyle. Even in a list of the great Frenchman Antoine Laurent Lavoisier (1743-1794), who is regarded as the founder of chemistry, side by side with real elements there also appear imponderable elements: a heat-producing and a light-producing substances.

In the first half of the 18th century, there were 15 known elements, and their number rose to 35 by the end of the century. True, only 23 of them were real elements, but the rest were either non-existent elements or else substances like caustic soda and caustic potash which turned out to be compounds.

By the middle of the 19th century, more than 50 undecomposable substances were described in chemical handbooks.

The periodic law of the great Russian chemist Dmitri Mendeleev (1834-1907) provided the stimulus for a conscious search for undiscovered elements. It is still too early to speak about this law here. Let us merely say that by means of his law Mendeleev showed how one must look for the elements which had not yet been discovered.

Almost all the elements occurring in nature were discovered by the beginning of the 20th century.

Atoms and Molecules

About 2000 years ago, an original poem was written in Ancient Rome. Its author was the Roman poet Lucretius. His poem was called *On the Nature of Things.*

With sonorous lines Lucretius told of the ancient Greek philosopher Democritus' views on the world in his poetic work.

What views were these? These were teachings about the minutest, invisible particles which our whole world is made of. Having observed various phenomena, Democritus tried to give them an explanation.

Take water, for example. When sufficiently heated, it evaporates and disappears. How can this be explained? It is clear that such a property of water is related to its internal structure.

Or why, for example, do we perceive the scent of flowers at a distance?

Meditating on similar questions, Democritus became convinced that bodies only seem to be solid, but in fact consist of the minutest particles. These particles are different in form for different bodies, but they are so small that they cannot be seen. That is why all bodies seem to us to be solid.

Democritus called such very tiny particles which cannot be further divided and of which water and all other bodies consist *atoms* (derived from the Greek *atomos* meaning "indivisible").

This remarkable guess of ancient Greek thinkers, born 24 centuries ago, was later long forgotten. Aristotle's erroneous teaching exercised complete sway over the scientific world for more than a thousand years.

Asserting that all substances are mutually transmutable, Aristotle categorically denied the existence of atoms. Any body can be infinitely divided, taught Aristotle.

In 1647, the Frenchman Pierre Gassendi (1592-1655) published a book in which he courageously denied Aristotle's teaching and asserted that all substances in the world consist of small indivisible particles—atoms. Atoms differ from each other in shape, size and mass.

Agreeing with the teachings of the ancient atomists, Gassendi developed these teachings further. He explained how the millions of diverse bodies of nature can and do arise in the world. For this, he asserted, a large number of different atoms is not necessary. For an atom is the same thing as building materials for houses. It is possible to construct an enormous number of the most diverse houses from three different kinds of building material—bricks, boards and logs. In precisely the same way, nature can create thousands of the most diverse bodies from several tens of different atoms. Moreover, in each body various atoms are united in small groups; Gassendi called these groups *molecules*, i.e. "small masses" (derived from the Latin *moles* meaning "mass").

Molecules of various bodies differ from each other in the number and kind ("sort") of atoms belonging to them. It is not difficult to understand that an immense number of different combinations of atoms, molecules, can be created from several tens of different atoms. This is why there is such a great variety in the bodies surrounding us.

However, Gassendi's views still contained much that was incorrect. Thus, he believed that there were special atoms for heat, cold, taste and smell. As other scientists of that time he too could not completely free himself from Aristotle's influence, and recognized his immaterial elements.

The following ideas experimentally verified much later are contained in the writings of M. V. Lomonosov, the great enlightener and founder of science in Russia.

Lomonosov writes that molecules can be homogeneous or heterogeneous. In the former case, similar atoms are grouped in a molecule. In the latter, a molecule consists of atoms differing from each other. If some body is composed of homogeneous molecules, it must be regarded as simple. If, on the contrary, a body consists of molecules built up from various atoms, Lomonosov calls it compound.

We now well know that nature's various bodies have precisely such a structure. In fact, take the gas oxygen for example; two identical atoms of oxygen are contained in each of its molecules. This is a molecule of a simple substance. But if the atoms composing a molecule are different, it is a chemical compound. Its molecules consist of atoms of those chemical elements which occur in the composition of this compound. This can also be said otherwise: each simple substance consists of atoms of one chemical element; a compound contains atoms of two or more elements.

A number of thinkers spoke about atoms, adducing logical arguments in favour of their existence. The English scientist John Dalton (1766-1844) introduced atoms into science in the right way and made them an object of research. Dalton showed that there exist chemical regularities which can be explained in a natural manner only by making use of the idea of an atom.

After Dalton, atoms firmly entered science. However, for a very long time there still were scientists who did not believe in atoms. Even at the very end of the last century, one of them wrote that after several decades it would be possible to find atoms only in the dust of libraries

Such reasoning seems funny now. We know now so many details about the "life" of an atom that to doubt its existence is the same thing as to doubt the reality of the Black Sea.

The relative masses of atoms were determined by chemists. At first the mass of a hydrogen atom was taken as the atomic mass unit. The relative atomic mass of nitrogen turned out to be approximately equal to 14, oxygen, approximately 16, chlorine, approximately 35.5. A somewhat different choice of the relative atomic mass units was later made, for which the number 16.0000 was assigned to oxygen. The atomic mass of hydrogen turned out equal to 1.008 in this scale.

Of interest, of course, is the absolute mass of atoms and not only their relative mass. It is sufficient, for this purpose, to measure the absolute mass of an atom of any one kind. Taken as the basis today is carbon rather than oxygen or hydrogen. Up to the present time, investigators regarded measurements of absolute masses of atoms with distrust and proceeded as follows. They took the mass of the carbon isotope ^{12}C to be equal to exactly twelve atomic mass units (amu). Then, paying no attention to the accuracy of measurement of the absolute masses of atoms, they assumed that

$$1\,\text{amu} = 1.662 \times 10^{-24}\,\text{g}$$

In any case, this value does not differ appreciably from the true one. Perhaps they are overcautious, however, since the precision of measurement today is within a fraction of about one-millionth. Measuring techniques have advanced greatly during the last century. In 1875, the known value of 1 amu was accurate within about 30 per cent.

How do we measure the mass of the atom in grams? No scales have been constructed, of course, on which a physicist could place a single atom and then balance it with a tiny weight. Like a hundred years ago, physicists use indirect experiments for this purpose today as well. They are not, however, in any way less reliable than direct weighing would be. But we cannot do without any weighing at all. We put a solid ball of carbon ^{12}C on the scale rather than a single atom (actually we proceed in a somewhat different way, but the point is to explain the idea of weighing and so we hope the informed reader forgives our simplified description). When the mass of the ball and its size are known, we can determine its density. The substance being weighed must be a perfect crystal. This is not easy to achieve, but more or less feasible. Hence, we can evidently write the following for the density found in the experiment

$$\rho = \frac{Zm_A}{V}$$

where m_A = mass of the atom in amu
V = volume of a unit cell of the crystal
Z = number of atoms per unit cell (see p. 61).

The last two quantities can be determined by X-ray structure analysis which is to be discussed in the fourth book.

The reader should not resent the fact that I seem to be getting ahead of my story. Books on physics should be read at least twice.

Employing this method, we can determine the atomic mass unit with exceptionally great precision. The most reliable value today is

$$1\ \text{amu} = (1.660\,43 \pm 0.000\,31) \times 10^{-24}\ \text{g}$$

We now ask the reader to use his imagination in order to grasp the minuteness of this value. Assume that you demand a thousand million molecules from each person on earth. How much matter can you collect in this way? Only several thousandths of a millionth of a gram.

Or another such comparison: the earth is as many times heavier than an apple as an apple is heavier than a hydrogen atom.

The reciprocal of the atomic mass unit is called *Avogadro's number*:

$$N_A = \frac{1}{1 \text{ amu}} = 6.022\,0943 \times 10^{23}$$

This enormous number has the following significance. Let us take a substance of an amount in grams equal to the relative mass M of its atoms or molecules, for example, 12 grams of the carbon isotope ^{12}C. This can be expressed more concisely: let us take one mole of a substance (check, please, with the definition of the mole given in the first book, where we introduced the International System of Units—SI units). The mass of one mole of a substance is equal to Mm_A. Consequently, the number of carbon atoms in 12 grams of carbon, as well as the number of atoms, molecules or any other particles in a mole assembly of these particles, equals

$$\frac{M}{Mm_A} = N_A$$

which is Avogadro's number.

For a long time physicists found no necessity for using the concept of the "amount of substance". As long as we dealt only with atoms and molecules it was quite suitable to define the mole as the molecular (or atomic) weight expressed in grams.

But then ions, electrons, mesons and many, many more particles made their appearance. Physicists came to the conclusion that it is not always convenient to characterize an assembly of particles by their mass. This led to the establishment of the unit for the amount of substance—the mole. When we speak of a mole of electrons, a mole of lead atom nuclei or a mole of pi-mesons, we are not specifying the mass of these particles (which, as you will find further on, depends upon their velocity), but only their number. The previous definition of a mole is still valid, however, because N_A atoms or molecules of any kind have a mass equal practically to the atomic or molecular mass expressed in grams. Neither has Avogadro's number changed its meaning; it simply has a new name: mole^{-1}.

What Heat Is

How does a hot body differ from a cold one? Up until the 19th century, this question was answered as follows: "A hot body contains more heat-producing matter (or 'caloric') than a cold one, in exactly the same sense as soup is saltier if it contains more salt." But what is caloric? The following answer was given to this question: "Caloric is the matter of heat, it is the elementary fire." Mysterious and incomprehensible. And this answer is in essence the same as the following explanation of what a rope is: "A rope is simple 'ropeness'."

Along with the caloric theory, a different view on the nature of heat had long been in existence. It was brilliantly advocated by many outstanding scientists of the 16-18th centuries.

Francis Bacon wrote in his book *Novum Organum*: "Heat itself in its essence is nothing but motion .... Heat consists of a variable motion of the minutest particles of a body."

Robert Hooke asserted in his book *Micrographia*: "Heat is a continuous motion of the parts of a body ...; There is no such body whose particles would be at rest."

We find particularly clear statements of this kind in Lomonosov's work (1745) *Reflections on the Cause of Heat and Cold*. The existence of caloric is denied in this work, where it is said that "heat consists of the internal motion of particles of matter".

Count von Rumford put it very graphically at the end of the 18th century: "The more intensively the particles composing a body move, the hotter the body will be, analogous to how the more vigorously a bell vibrates, the louder it rings."

In these remarkable guesses, far ahead of their time, the bases of our modern views on the nature of heat are concealed.

There are sometimes quiet and clear days. The leaves lie still on the trees, not even a slight ripple disturbs the glassy surface of water. The entire surroundings have frozen in strict, triumphant immobility. The visible world is at rest. But what is taking place in the world of atoms and molecules?

Contemporary physicists can say much about this. Never, not under any circumstances, is there a cessation to the invisible motion of the particles that the world is made of.

But why don't we see all these motions? Particles move, but the body is stationary. How is this possible?

Have you ever watched a swarm of midges? When there is no wind, the swarm appears to be suspended in air. But an intensive life is going on inside the swarm. Hundreds of insects flew off to the right, but just as many flew off to the left at the same instant. The swarm as a whole remained at the same place and did not change its form.

The invisible motions of atoms and molecules are of the same chaotic, irregular nature. If some molecules leave a volume, their place is occupied by others. But since the newcomers do not in the least differ from the departed molecules, the body remains entirely as it was. An irregular, chaotic motion of particles does not change the properties of the visible world.

"However, isn't this idle talk?" the reader might ask us. In what sense are these arguments, however beautiful, more convincing than the caloric theory? Has anyone actually seen the eternal thermal motion of particles of matter?

It is possible to see the thermal motion of particles and, moreover, with the aid of the simplest microscope. This phenomenon was first observed more than a hundred years ago by the English botanist Robert Brown (1773-1858).

Looking at the internal structure of a plant through a microscope, he noticed that tiny particles of matter floating in the sap of the plant were continually moving in all directions. The botanist became interested: what forces made the particles move? Perhaps they were living beings of some kind? The scientist decided to examine under a microscope small particles of clay making some water turbid. But neither were these undoubtedly lifeless particles at rest; they were engaged in a continual and chaotic motion. The smaller the particles were, the faster they moved. The botanist examined this drop of water for a long time, but still he couldn't see any end to the motion of the particles. Some invisible forces seemed to be constantly pushing them.

The Brownian movement of particles is just a thermal motion. Thermal motion is inherent in large and small particles, clots of molecules, individual molecules and atoms.

Energy Is Conserved Forever

Thus, the world is composed of moving atoms. Atoms possess mass, moving atoms possess kinetic energy. Of course, the mass of an atom is unimaginably small, and so its energy will also be minute, but there are millions of millions of millions of atoms.

We now remind the reader that although we spoke of the law of conservation of energy, this was not a sufficiently universal conservation law. Linear and angular momenta were conserved experimentally, but energy was only conserved ideally—in the absence of friction. But as a matter of fact, energy always decreased.

But we did not say anything previously about the energy of atoms. A natural idea arises: where at first sight we noticed a decrease in energy, some energy was transmitted to the atoms of a body in a manner which is imperceptible to the naked eye.

Atoms are subject to the laws of mechanics. True (you will have to learn this from another book), their mechanics is somewhat peculiar, but this does not change matters—with respect to the law of conservation of mechanical energy, atoms do not differ at all from large bodies.

Hence, the complete conservation of energy will be detected only when along with the mechanical energy of a body the internal energy of this body and the environment is taken into account. Only in this case will the law be universal.

What does the total energy of a body consist of? We have, in essence, already named its first component—it is the sum of the kinetic energies of all its atoms. But it must not be forgotten that atoms interact with each other. Therefore, the potential energy of this interaction is added. Thus, the total energy of a body is equal to the sum of the kinetic energies of its particles and the potential energy of their interaction.

It is not difficult to comprehend that the mechanical energy of a body as a whole is only part of its total energy. For when a body is stationary, its molecules do not stop moving and do not cease interacting with each other. The energy of the thermal motion of particles which remains in a stationary body and the energy

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of the interaction between the particles constitute the internal energy of the body. The total energy of a body is therefore equal to the sum of its mechanical and internal energies.

The gravitational energy of a body is a component part of its mechanical energy, i.e. the potential energy of the interaction between its particles and the Earth.

Considering internal energy, we no longer detect vanishing of energy. When we consider nature through glasses magnifying the world millions of times, the picture seems to us to be of rare harmoniousness. There are no losses of mechanical energy, but there is only its transformation into the internal energy of a body or its surroundings. Has any work disappeared? No! The energy went into an acceleration of the relative motion of molecules or a change in their mutual distribution.

Molecules obey the law of conservation of mechanical energy. There are no frictional forces in the world of molecules; the world of molecules is controlled by transformations of potential energy into kinetic one and vice versa. Only in the coarse world of large objects, which does not notice molecules, does "energy vanish".

If mechanical energy totally or partially vanishes during some occurrence, the internal energy of the bodies and media participating in this occurrence will grow by the same amount. Putting it otherwise, mechanical energy is transformed without any loss whatsoever into the energy of molecules or atoms.

The law of conservation of energy is the strictest "bookkeeper" of physics. The income and outgo of energy should exactly balance during any occurrence. If this did not take place in some experiment, this implies that something important escaped our attention. In such a case, the law of conservation of energy gives us a signal: researcher, repeat the experiment, increase the accuracy of your measurements, look for the cause of the loss! Physicists have repeatedly made new, important discoveries along these lines, convincing themselves time and time again of the perfectly strict validity of this remarkable law.

Calorie

We already have two units of energy—the erg and the kilogram-force-metre. It would seem that this is enough. However, it is traditional to employ yet a third unit—the *calorie*—in the study of thermal phenomena.

We shall see later that even with the calorie the list of units adopted for designating energies is not exhausted.

It is possible that in each individual case the use of its "own" unit of energy is convenient and expedient. But in any example which is the least bit complicated, dealing with the transformation of energy from one form to another, an inconceivable mix-up with units arises.

In order to simplify computations, the system of units (SI) provides for a single unit for work, energy and an amount of heat—the joule. However, considering the strength of tradition and the length of time which will be required for this system to become the only system of units in general use, it is helpful to acquaint ourselves more closely with the "departing" unit of heat—the calorie.

The *small calorie* (cal) is the amount of heat required to raise the temperature of one gram of water from 14.5 to 15.5 °C. The word "small" must be mentioned because one sometimes uses the "large" calorie, which is a thousand times as great as the chosen unit (the *large calorie* is often denoted by kcal, which means "kilocalorie").

The relationship between a calorie and mechanical units of work, such as an erg or a kilogram-force-metre, is found by heating water mechanically. Such experiments have been performed repeatedly. It is possible, for example, to raise the temperature of water by stirring it energetically. The mechanical work expended for the heating can be evaluated with sufficient accuracy. It was found from such measurements that

$$1 \text{ cal} = 0.427 \text{ kgf-m} = 4.18 \text{ J}$$

Since energy and work have units in common, it is also possible to measure work in calories. One must expend 2.35 calories in order to raise a kilogram weight by one metre. This sounds unusual, and it really is inconvenient to compare the raising of a load with the heating of water. Therefore, calories are not employed in mechanics.

Some History

The law of conservation of energy could only be formulated when the idea of the mechanical nature of heat had become sufficiently clear and when technology had posed in practice the important question of the equivalence between heat and work.

The first experiment establishing a quantitative relationship between heat and work was carried out by the well-known physicist Sir Benjamin Thompson (Count von Rumford) (1753-1814). He worked in a factory where cannon were manufactured. When the muzzle of a gun is bored, heat is liberated. How could it be estimated? What should be taken as the measure of heat? It occurred to Rumford to relate the work performed in boring with the heating of one or another amount of water by one or another number of degrees. This investigation was perhaps the first precise expression of the idea that heat and work should have a measure in common.

The next step towards the discovery of the law of conservation of energy was the establishment of an important fact: a disappearance of work is accompanied by an appearance of a proportional amount of heat; thus a common measure for heat and work was found.

The original definition of the so-called mechanical equivalent of heat was given by the French physicist Sadi Carnot (1796-1832). This outstanding person died at the age of 36 in 1832 and left behind a manuscript, which was published only after 50 years. The discovery made by Carnot remained unknown and did not influence the development of science. Carnot calculated in this work that the raising of 1 m^3 of water to a height of 1 m requires just as much energy as is needed for the heating of 1 kg of water by 2.7 degrees (the correct figure is 2.3 degrees).

The Heilbronn doctor Julius Robert von Mayer (1814-1878) published his first work in 1842. Although Mayer called physical concepts familiar to us by entirely different names, a careful reading of his work leads nevertheless to the conclusion that the essential features of the law of conservation of energy are presented in it. Mayer distinguished between the internal energy ("thermal"), gravitational potential energy and energy of motion of a body. He tried to infer the necessity of conservation of energy under various transformations from purely theoretical considerations. In order to check this assertion experimentally, one must have a common measure for measuring these energies. Mayer calculated that the heating of 1 kg of water by one degree is equivalent to the raising of 1 kg by 365 m.

In his second work published three years later, Mayer noted the universality of the law of conservation of energy—the possibility of applying it to questions of chemistry, biology and cosmic phenomena. To the various known forms of energy Mayer added magnetic, electric and chemical.

A lot of credit for the discovery of the law of conservation of energy goes to the remarkable English physicist (a brewer from Salford in England) James Prescott Joule (1818-1889), working independently of Mayer.

While a certain inclination to an indeterminate philosophy is characteristic of Mayer, Joule's basic trait is a strict experimental approach towards the phenomena under consideration. Joule posed a question before nature and obtained an answer to it by means of special experiments set up in an exceptionally painstaking manner. There is no doubt that in the entire series of experiments performed by Joule, he was guided by a single idea—to find a common measure for evaluating thermal, chemical, electrical and mechanical actions, to demonstrate that energy is conserved in all these phenomena. Joule formulated his idea as follows: "The destruction of forces performing work does not occur in nature without a corresponding action."

Joule reported on his first work on January 24, 1843, and on August 21 of the same year, he communicated his results on the establishment of a common measure for heat and work. Heating 1 kg of water by one degree proved equivalent to raising 1 kg by 460 m.

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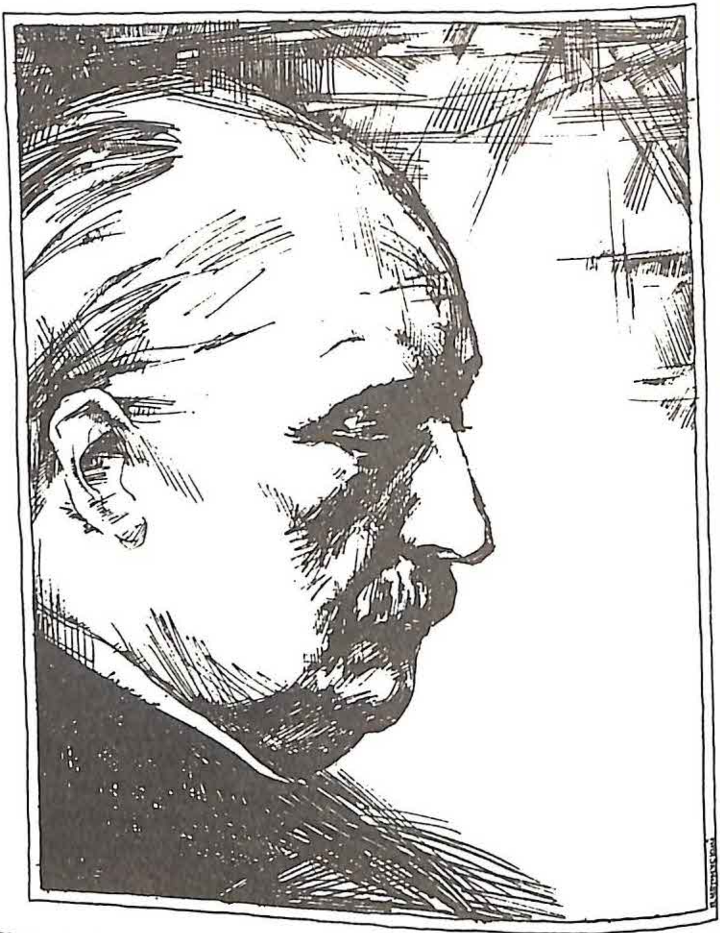

Hermann Helmholtz (1821-1894)—a famous German scientist. Helmholtz worked in the fields of physics, mathematics and physiology with great success. He was the first (1847) to give a mathematical interpretation of the law of conservation of energy emphasizing the universal character of this law. Helmholtz obtained outstand-

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A lot of credit for the discovery of the law of conservation of energy goes to the remarkable English physicist (a brewer from Salford in England) James Prescott Joule (1818-1889), working independently of Mayer.

While a certain inclination to an indeterminate philosophy is characteristic of Mayer, Joule's basic trait is a strict experimental approach towards the phenomena under consideration. Joule posed a question before nature and obtained an answer to it by means of special experiments set up in an exceptionally painstaking manner. There is no doubt that in the entire series of experiments performed by Joule, he was guided by a single idea—to find a common measure for evaluating thermal, chemical, electrical and mechanical actions, to demonstrate that energy is conserved in all these phenomena. Joule formulated his idea as follows: "The destruction of forces performing work does not occur in nature without a corresponding action."

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In the following years, Joule and a number of other researchers spent a great deal of effort in order to find a more precise value for the thermal equivalent, and also attempted to prove the complete universality of the equivalent. During the late forties, it became clear that, regardless of how work is transformed into heat, the amount of heat arising will always be proportional to the amount of work expended. In spite of the fact that Joule laid the experimental basis for the law of conservation of energy, he did not give a clear formulation of this law in his works.

The credit for this belongs to the German physicist Hermann Helmholtz. On July 23, 1847, at a meeting of the Berlin Physical Society, Helmholtz gave a lecture on the principle of conservation of energy. The mechanical basis of the law of conservation of energy was clearly presented for the first time in this talk. The world consists of atoms; atoms possess potential and kinetic energies. The sum of the potential and kinetic energies of the particles which a body or system is made of cannot change, if the body or system is not subjected to external influences. The law of conservation of energy, as we outlined it several pages above, was first formulated by Helmholtz.

After the work of Helmholtz, it remained for other physicists to merely verify and apply the law of conservation of energy. The success of these investigations led to the fact that by the end of the fifties the law of conservation of energy was universally recognized as a fundamental law of natural science.

Phenomena casting doubt on the law of conservation of energy have already been observed in the 20th century. However, explanations were later found for the apparent discrepancies. The law of conservation of energy has so far always stood the test with credit.

2. Structure of Matter

Intramolecular Bonds

Molecules consist of atoms. Atoms are bound in molecules by forces which are called chemical forces.

There exist molecules consisting of two, three, four atoms. The largest molecules, protein molecules, consist of tens and even hundreds of thousands of atoms.

The molecule kingdom is exceptionally varied. By now, millions of substances built up out of various molecules have already been isolated by chemists from natural materials and created in their laboratories.

Properties of molecules are determined not only by how many atoms of one or another sort participate in their construction but also by the order and configuration in which they are bound. A molecule is not a heap of bricks, but a complicated architectural structure, where each brick has its place and its completely determined neighbours. The atomic structure forming a molecule can be rigid to a greater or lesser degree. In any case, each of the atoms carries out an oscillation about its equilibrium position. In certain cases, some parts of a molecule can even revolve around other parts giving different and the most fantastic configurations to a free molecule in the process of its thermal motion.

Let us analyze the interaction between atoms in greater detail. The potential energy curve of a diatomic molecule is depicted in Figure 2.1. It has a characteristic form—it first goes down, then turns up forming a "well", and afterwards rises more slowly towards the horizontal axis on which the distance between the atoms is marked.

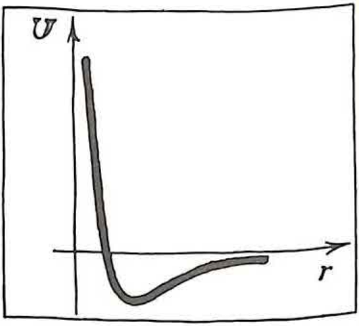

Figure 2.1

We know that the state in which the potential energy has the minimum value is stable. When an atom forms a part of a molecule, it "sits" in a potential well, carrying out small thermal oscillations about its equilibrium position.

The distance from the vertical axis to the bottom of the well can be called the equilibrium distance. The atoms would be located at this distance if the thermal motion were to cease.

The potential energy curve tells about all the details of the interaction between atoms. Whether particles attract or repel each other at one or another distance, whether the strength of the interaction increases or decreases when the particles separate or approach all this information can be obtained from the analysis of the potential energy curve. Points to the left of the "bottom" of the well correspond to repulsion. On the contrary, points to the right of the bottom of the well characterize attraction. The steepness of the curve also yields important information: the steeper the curve, the greater the force.

When atoms are at great distances from each other, they are attracted; this force decreases rather rapidly with an increase in the distance between them. As they approach each other, the force of attraction grows and reaches its maximum value when the atoms come very close to each other. As they come even closer, the attraction weakens and, finally, at the equilibrium distance the force of the interaction vanishes. When the atoms become closer than the equilibrium distance, forces of repulsion arise which sharply increase and quickly make a further decrease in the distance between the atoms practically impossible.

Equilibrium distances (below we shall say distances for the sake of brevity) between atoms are different for various types of atoms.

For various pairs of atoms, not only are the distances between the vertical axis and the bottom of the well different but so are the depths of the wells.

The depth of a well has a simple meaning: in order to roll out of the well, an energy just equal to the depth is needed. Therefore, the depth of a well can be called the binding energy of the particles.

The distances between the atoms of a molecule are so small that it is necessary to choose appropriate units for their measurement; otherwise, their values would have to be expressed, for example, in the following form: 0.000 000 012 cm. This figure is for an oxygen molecule.

Units especially convenient for describing the atomic world are called *angstroms* (true, the name of the Swedish scientist in whose honour these units were named is properly spelt Angström; in order to remember this, a small circle is placed over the letter A);

$$1\ \text{Å} = 10^{-8}\ \text{cm}$$

i.e. one-hundred-millionth of a centimetre.

The distances between the atoms of a molecule lie within the limits of 1 to 4 A. The equilibrium distance for oxygen, which has been written out above, is equal to 1.2 Å.

Interatomic distances, as you see, are very small. If we gird the Earth with a string at the equator, then the length of the "belt" will be as many times greater than the width of your palm as the latter is greater than the distance between the atoms of a molecule.

Ordinary calories are used for measuring binding energies, but they are related not to one molecule, which would, of course, yield a negligible number, but to one mole, i.e. to the number of grams equal to the relative molecular mass.

It is clear that the binding energy per mole divided by Avogadro's number, $N_A = 6.023 \times 10^{23}\ \text{mol}^{-1}$, yields the binding energy of a single molecule.

The binding energy of the atoms in a molecule, just as interatomic distances, varies within narrow limits.

For the same oxygen, the binding energy is equal to 116 000 cal/mol, for hydrogen 103 000 cal/mol, etc.

We have already said that the atoms in a molecule are distributed in an entirely definite manner with respect to each other, forming in complicated cases rather intricate structures.

Let us present several simple examples. In a molecule of CO_2 (carbon dioxide), all three atoms are lined up in a row, with the carbon atom in the middle. A molecule of H_2O (water) has an angular form, with the oxygen atom at the vertex of the angle (it is equal to 105°).

In a molecule of NH_3 (ammonia), the nitrogen atom is at the vertex of a three-faced pyramid, in a molecule of CH_4 (methane), the carbon atom is located at the centre of a four-faced figure with equal sides, which is called a tetrahedron.

The carbon atoms of C_6H_6 (benzene) form a regular hexagon. The bonds of the carbon atoms with the hydrogen atoms go from all the vertices of the hexagon. All the atoms are situated in one plane.

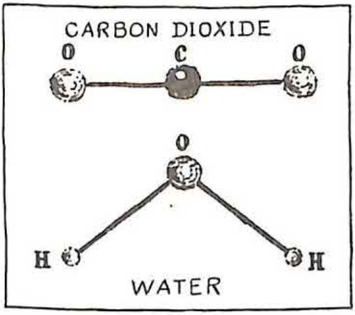

Figure 2.2

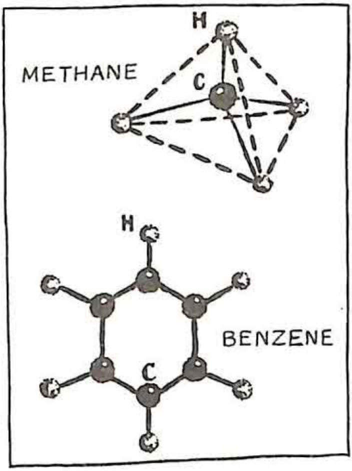

Figure 2.3

Diagrams of the distribution of the centres of the atoms in these molecules are shown in Figures 2.2 and 2.3. The lines symbolize the bonds.

A chemical reaction occurred; there were molecules of one type, and then others were formed. Some bonds were broken, while others were newly created. In order to break the bonds between atoms (recall Figure 2.1) it is necessary to perform work, just as in rolling a ball out of a well. On the contrary, energy is liberated when new bonds are formed, just as when a ball rolls into a well.

Which is greater, the work involved in breaking or in creating bonds? We come across reactions of both types in nature.

The excess energy is called the *thermal effect*, or more concisely, the *heat of transformation* (*reaction*). The heat of reaction is usually a quantity of the order of tens of thousands of calories per mole. The heat of reaction is often included as a summand in the formula for a reaction.

For example, the reaction whereby carbon in the form of graphite burns, i.e. unites with oxygen, is written out as follows:

$$C + O_2 = CO_2 + 94\,250 \text{ cal}$$

This means that when carbon combines with oxygen an energy of 94 250 calories is liberated.

The sum of the internal energies of a mole of carbon and a mole of oxygen is equal to the internal energy of a mole of carbon dioxide plus 94 250 calories.

Thus, such formulas have the transparent meaning of algebraic equalities written in terms of the values of the internal energies.

With the aid of such equations, one can find the heats of reaction for which direct methods of measurement, as a result of one or another cause, are unsuitable. Here is an example: if carbon (graphite) were to combine with hydrogen, the acetylene would be formed:

$$2C + H_2 = C_2H_2$$

The reaction does not proceed in this manner. Nevertheless, it is possible to find its thermal effect. We write down three known reactions:

(1) the oxidation of carbon

$$2C + 2O_2 = 2CO_2 + 188\,000 \text{ cal}$$

(2) the oxidation of hydrogen

$$H_2 + \frac{1}{2} O_2 = H_2O + 68\,000 \text{ cal}$$

(3) the oxidation of acetylene

$$C_2H_2 + \frac{5}{2} O_2 = 2CO_2 + H_2O + 312\,000 \text{ cal}$$

All these equalities may be regarded as equations for the binding energies of molecules. If so, we may operate on them as on algebraic equalities. Subtracting the first two equalities from the third, we obtain:

$$2C + H_2 = C_2H_2 - 56\,000\ \text{cal}$$

Therefore, the reaction we are interested in is accompanied by the consumption of 56 000 calories per mole.

Physical and Chemical Molecules

Until investigators had formed a detailed concept of the structure of matter, no such distinction was made. A molecule was simply a molecule, i.e. the smallest representative of a substance. It seemed that nothing more could be said. This is not so, however.

The molecules we have just discussed are molecules in both senses of the word. Molecules of carbon dioxide, ammonia and benzene (mentioned above), and the molecules of practically all organic substances (which were not discussed) consist of atoms strongly bonded to one another. These bonds are not ruptured by dissolution, melting or evaporation. The molecule continues to behave as a separate particle or small physical body upon any physical action or change in state.

But this is not always true. For most inorganic substances, we can speak of the molecule only in the chemical sense. The finest particles of such well-known inorganic substances as common salt or calcite or soda do not even exist. We do not find separate particles of these substances in crystals (this will be discussed a few pages further on); when they are dissolved, the molecules break down into their component atoms.

Sugar is an organic substance. Therefore, the sugar dispersed in a cup of sweetened tea is in the form of molecules. Salt is a different matter. We find no molecules of common salt (sodium chloride) in salty water. These "molecules" (we have to use quotation marks) exist in water in the form of atoms (actually, ions—electrically charged atoms—that will be discussed later).

The same is true of vapours; and in melts a part of the molecules live their own independent lives.

When we speak of the forces binding the atoms together in a physical molecule, we call them valence forces. Intermolecular forces are not of the valency kind. The general shape of the interaction curve, of the type illustrated in Figure 2.1, is the same for both kinds of forces. The difference lies in the depth of the potential well. For valence forces the well is hundreds of times deeper.

Interaction of Molecules

There can be no doubt of the fact that molecules attract each other. If they stopped doing so for an instant, all liquids and solids would decompose into molecules.

Molecules repel each other, and neither can this be doubted, because liquids and solids would otherwise contract with extraordinary ease.

Forces are exerted between molecules which resemble in many respects the forces between atoms spoken of above. The potential energy curve which we have just drawn for atoms gives a true picture of the basic features of molecular interaction. However, there are also essential differences between these interactions.

Let us compare, for example, the equilibrium distances between oxygen atoms forming a molecule and oxygen atoms of two neighbouring molecules attracted in solidified oxygen before the equilibrium position. The difference will be very noticeable: the oxygen atoms forming a molecule settle down at a distance of 1.2 Å, while the oxygen atoms of different molecules approach each other to within 2.9 Å.

Analogous results have also been obtained for other atoms. Atoms of different molecules settle down farther from each other than atoms of the same molecule. It is therefore easier to tear molecules apart from each other than atoms from a molecule; moreover, the difference in energy is much greater than that in distance. While the energy necessary for breaking the bonds between oxygen atoms forming a molecule is about 100 kcal/mol, the energy needed to pull oxygen molecules asunder is less than 2 kcal/mol.

Hence, on a potential energy curve for molecules, the potential well lies farther away from the vertical axis and, furthermore, the well is much shallower.

However, this does not exhaust the difference between the interaction between atoms forming a molecule and the interaction of molecules.

Chemists have shown that atoms are bound in a molecule with a fully determined number of other atoms. If two hydrogen atoms have formed a molecule, no third atom will join them to this end. An oxygen atom in water is bound to two hydrogen atoms, and it is impossible to bind another atom to them.

We do not find anything similar in intermolecular interaction. Having attracted one neighbour to itself, a molecule does not lose its "attractive force" to any degree. The approach of neighbours will continue as long as there is enough room.

What does "there is enough room" mean? Are molecules really something like apples or eggs? Of course, in a certain sense such a comparison is justified: molecules are physical bodies possessing definite size and shape. The equilibrium distance between molecules is nothing but their size.

What Thermal Motion Looks Like

The interaction between molecules can have greate or smaller values during the "lives" of the molecules.

The three states of matter—gaseous, liquid and solid—differ from one another in the role which molecular interaction plays in them.

The word "gas" was thought up by scientists (derived from the Greek *chaos* meaning "disorder").

And as a matter of fact, the gaseous state of matter is an example of the existence in nature of complete, perfect disorder in the mutual distribution and motion of particles. There is no microscope which would permit one to see the motion of gaseous molecules, but in spite of this, physicists can describe the life of this invisible world in sufficient detail.

There is an enormous number of molecules, approximately 2.5×10^{19} molecules in a cubic centimetre of air under standard conditions (room temperature and atmospheric pressure). Each molecule's share is a volume of 4×10^{-20} cm^3, that of a small cube whose sides are approximately 3.5×10^{-7} cm = 35 Å. However, the molecules are much smaller. For example, molecules of oxygen and nitrogen—the basic components of air—have an average size of about 4 Å.

Therefore, the average distance between molecules is ten times as great as the size of the molecules. And this in turn implies that the average volume of air per molecule is approximately a thousand times as great as the volume of the molecule itself.

Imagine a plane surface on which coins have been thrown in a random manner, where there is an average of a hundred coins to each square metre. This means one or two coins on a page of the book which you are reading. This is roughly how sparsely gas molecules are distributed.

Every molecule of a gas is in a state of continual thermal motion.

Let us follow a single molecule. Here it is swiftly moving somewhere to the right. If it met no obstacles in its path, the molecule would continue its motion with the same velocity along a straight line. But the path of the molecule is crossed by its innumerable neighbours. Collisions are inevitable, and the molecules fly apart like two colliding billiard balls. In which direction will our molecule gallop? Will it acquire or lose its speed? Anything is possible: for its collisions can be of the most various kinds. Blows are possible from the front or from behind, from the right or the left, which are strong or weak. It is clear that being subject to such irregular impacts during these random collisions, the molecule which we are observing will rush about through all parts of the vessel in which gas is confined.

How far are gas molecules able to go without a collision?

It depends on the size of the molecules and the density of the gas. The larger the molecules and the more molecules there are in a vessel, the more often will they collide. The average distance travelled by a molecule without any impact—it is called the mean free path—is equal to 11×10^{-6} cm $=$ 1100 Å for hydrogen molecules and 5×10^{-6} cm $=$ 500 Å for oxygen molecules under ordinary conditions. The distance of 5×10^{-6} cm (one-twenty-thousandth of a millimetre) is very small, but it is far from small in comparison with molecular sizes. A distance of 10 m for a billiard ball corresponds in scale to a path of 5×10^{-6} cm for an oxygen molecule.

The structure of a liquid differs essentially from that of a gas whose molecules are far from each other and only rarely collide. In a liquid, a molecule is constantly found in the immediate vicinity of others. The molecules of a liquid are distributed like potatoes in a sack. True, with one distinction: the molecules of a liquid are in a state of continual and chaotic thermal motion. Because they are so crowded, they cannot move around as freely as the molecules of a gas. Each of them is always "marking time" in practically one and the same place surrounded by the same neighbours, and only gradually moves through the volume occupied by the liquid. The more viscous the liquid, the slower this displacement. But even in such a "mobile" liquid as water, a molecule moves 3 Å during the time required by a gas molecule to cover 700 Å.

The forces of interaction between molecules deal very resolutely with their thermal motion in solids. In solid matter, the molecules are almost always in a fixed position. The only effect of the thermal motion is that the molecules are continually vibrating about their equilibrium positions. The lack of systematic displacements by the molecules is precisely the cause of what we call solidity. In fact, if molecules do not change neighbours, all the more will the separate parts of the body remain in a fixed bond with one another.

Compressibility of Bodies

As raindrops drum on a roof, so do gas molecules beat against the walls of a vessel. The number of these blows is immense, and it is their united action that creates the pressure which can move the piston of an engine, explode a shell or blow up a balloon. A hail of molecular blows—this is atmospheric pressure, this is the pressure that makes the lid of a boiling tea-kettle jump, this is the force driving a bullet out of a rifle.

What is gas pressure related to? It is clear that the stronger the blow inflicted by a single molecule, the greater the pressure. It is no less obvious that the pressure will depend on the number of blows inflicted in a second. The more molecules in a vessel, the more frequent the blows and the greater the pressure. Hence, the pressure p of a given gas is proportional, first of all, to its density.

If the mass of a gas is constant, then decreasing its volume, we increase its density by the corresponding factor. Therefore, the pressure of a gas in a closed vessel will be inversely proportional to its volume. Or, in other words, the product of the pressure by the volume must be constant:

$$pV = \text{const}$$

This simple law was discovered by the English physicist Robert Boyle (1627-1691) and the French scientist Edme Mariotte (*c.* 1620-1684). *Boyle's law* (also known as *Mariotte's law*) is one of the first quantitative laws in the history of physical science. Of course, it holds when the temperature is constant.

As a gas is compressed, the Boyle equation is satisfied worse and worse. The molecules approach each other and the interactions between them begin to influence the behaviour of the gas.

Boyle's law is valid in those cases when the interference of the forces of interaction between the gas molecules is completely insignificant. One therefore speaks of Boyle's law as a law of ideal gases.

The adjective "ideal" sounds rather funny when modifying the word "gas". Ideal means perfect, so that it is impossible to be better.

The simpler a model or diagram, the more ideal it is for the physicist. Computations are simplified, explanations of physical phenomena become easy and clear. The term "ideal gas" pertains to the simplest model of a gas. The behaviour of sufficiently rarefied gases is practically indistinguishable from that of ideal gases.

Liquids are much less compressible than gases. In a liquid, the molecules are already in "contact". Compression consists only in improving the "packing" of the molecules, and for very high pressures, in pressing the molecules themselves. The degree to which the forces of repulsion hinder the compression of a liquid can be seen from the following figures. A rise in pressure from one to two atmospheres entails a decrease in the volume of a gas by a factor of two, while the volume of water changes by 1/20 000, and that of mercury by a total of 1/250 000.

Even the enormous pressure in the depths of an ocean is incapable of compressing water to any noticeable extent. In fact, a pressure of one atmosphere is created by a ten-metre column of water. The pressure under a 10-km layer of water is equal to 1000 atm. The volume of water decreases by 1000/20 000, i.e. by one-twentieth.

The compressibility of solids differs little from that of liquids. This is understandable since in both cases the molecules are already in contact, and so compression can only be achieved at the expense of a further drawing together of molecules which are already strongly repelling each other. By means of ultrahigh pressures of 50-100 thousand atmospheres, we are able to compress steel by one-thousandth, and lead by one-seventh, of its volume.

It is clear from these examples that, under terrestrial conditions, we cannot succeed in compressing solid matter to any significant extent.

But in the Universe, there are bodies where matter is compressed with incomparably greater strength. Astronomers discovered the existence of stars in which the density of matter reaches 10^6 g/cm^3. Inside these stars, called white dwarfs ("white" for the nature of their luminosity, "dwarfs" because of their relatively small size), there should therefore be enormous pressures.

Surface Tension

Is it possible to emerge dry from water? Of course it is, if one smears oneself with a non-wettable substance.

Rub your finger with paraffin and put it under water. When you take it out, you will find that except for two or three drops there is no water on your finger. A slight motion—and the drops are shaken off.

In this case we say that water does not wet paraffin. Mercury behaves in such a manner towards almost all solid bodies: it does not wet leather, glass or wood.

Water is more capricious. It adheres closely to some bodies and tries not to touch others. Water does not wet oily surfaces, but thoroughly wets clean glass. Water wets wood, paper and wool.

If a drop of water is placed on a clean plate of glass, it will spread out and form a very shallow, small puddle. If such a drop is put on a piece of paraffin, it will just remain a drop, almost spherical in shape and slightly flattened by gravity.

Among the substances which "stick" to almost all bodies is kerosene. Striving to flow along glass or metal, kerosene is capable of creeping out of a loosely closed vessel. A puddle of spilled kerosene can spoil one's existence for a long time: kerosene will seize a large surface, creep into cracks and penetrate one's clothes. That is why it is so difficult to get rid of its not very pleasant odour.

The failure to wet bodies can lead to curious phenomena. Take a needle, grease it and carefully place it flat on water. The needle will not sink. Looking attentively, you can notice that the needle depresses the water and calmly lies in the small hollow so formed. However, a slight pressure is enough to make the needle go to the bottom. For this it is necessary that a considerable part of it turns out to be in the water.

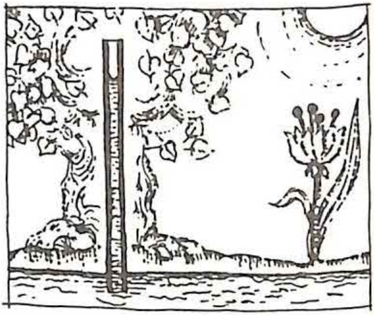

Figure 2.4

This interesting property is made use of by water striders running swiftly along the surface of the water without wetting their feet.

Wetting is used to dress ores by means of floatation. The word "floatation" means "surfacing". The essence of the phenomenon is as follows. Finely crushed ore is loaded into a vat containing water. A small amount of special oil is added; this oil must wet the particles of the mineral and not wet the particles of the gangue (this is what the valueless rock or aggregates of minerals in an ore are called). When mixed, the particles of the mineral are coated with an oily film.

Air is blown into the black mixture of ore, water and oil. There is formed a mass of little bubbles of air—foam. The air bubbles come to the surface. The process of floatation is based on the fact that the particles covered with oil cling to the air bubbles. A large bubble carries up a small particle like a balloon.

The mineral collects at the surface in the form of foam and the gangue remains at the bottom. The foam is removed and sent for further processing in order to obtain a so-called "concentrate", which contains tens of times as little gangue.

Forces of cohesion between surfaces are capable of violating the levelling of a liquid in communicating vessels. It is very easy to verify the truth of this.

If a thin glass tube (with a diameter of a fraction of a millimetre) is lowered into water, then in violation of the law of communicating vessels, the water in it will quickly begin rising, and its level will become considerably higher than in the large vessel (Figure 2.4).

But what took place? What forces are supporting the weight of the column of liquid that has risen up? The rise is accomplished by the forces of cohesion between the water and the glass.

Forces of cohesion between surfaces clearly manifest themselves only when a liquid rises in a sufficiently thin tube. The narrower the tube, the higher the liquid and the more distinct the phenomenon. The name of these surface phenomena is related to the name of the tubes. The inside diameter of such a tube is measured in fractions of a millimetre, such a tube is called capillary (meaning "thin as a hair"). The phenomenon of the rise of liquids in thin tubes is called capillarity.

But to what height are capillary tubes capable of raising a liquid? It turns out that water rises to a height of 1.5 mm in a tube of 1-mm diameter. For a diameter of 0.01 mm, the height of the rise will increase as many times as the diameter of the tube decreases, i.e. to 15 cm.

Of course, the elevation of a liquid is possible only in the case of wetting. It is not hard to guess that mercury will not rise in glass tubes. On the contrary, mercury falls in glass tubes. Mercury is so "intolerant" of contact with glass that it strives to reduce the total surface to the minimum allowed by gravity.

There exist many bodies which are something like systems of very thin tubes. Capillary phenomena can always be observed in such bodies.

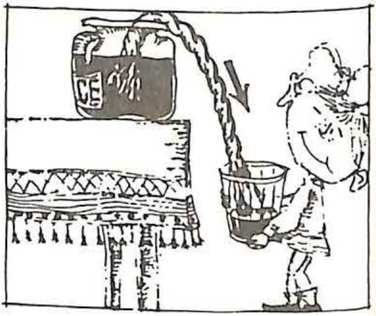

Figure 2.5

Plants and trees have an entire system of long ducts and pores. The diameters of these ducts are less than hundredths of a millimetre. Because of this, capillary forces raise soil moisture to a considerable height and distribute water throughout the plant.

Blotting paper is a very convenient thing. You spilled some ink on a page and want to turn it over. But you're not going to wait until the blot dries up. You take a sheet of blotting paper, dip one of its edges in the drop, and the ink swiftly runs upwards against gravity.

A typical capillary phenomenon has occurred. If you look at the blotting paper through a microscope, you can see its structure. Such a paper consists of a sparse network of paper fibres forming thin and long ducts with each other. These ducts play the role of capillary tubes.

The same kind of system of long pores or ducts formed by fibres exists in wicks. Kerosene rises through the wick of a lamp. A siphon can also be created with the aid of a wick by placing one of its ends in a glass partially filled with water, in such a way that the other end hanging over the edge is lower than the first (Figure 2.5).

In the technology of the dyeing industry, frequent use is also made of the ability of a fabric to draw in a liquid through the thin pores formed by the *threads* of the fabric.

We have not said anything yet about the molecular mechanism of these interesting phenomena.

The differences in the surface tension of various substances can be excellently explained by intermolecular interactions.

A drop of mercury does not spread out over the surface of glass. The reason is that the energy of interaction between the mercury atoms is greater than the energy of cohesion between the glass and mercury atoms. For the same reason, mercury does not rise in narrow capillary tubes.

It is a different matter with water. It was found that the atoms of hydrogen of the water molecules readily cohere to the atoms of oxygen in the silica of which glass mainly consists. The water-glass intermolecular forces are greater than the water-water intermolecular forces. Therefore, water spreads out into a thin film over the surface of glass and rises in glass capillary tubes.

Surface tension or, more precisely, the energy of cohesion (depth of the potential well in Figure 2.1) for various pairs of substances can be both measured and calculated. A discussion on how this can be done would lead us too far away from our subject.

Crystals and Their Shape

Many people think that crystals are beautiful, rarely found stones. They occur in various colours, are usually transparent and, what is most remarkable, possess a beautiful regular shape. Crystals are most often polyhedra with ideally plane sides (faces) and strictly straight edges. They please the eye with a marvellous play of colours at the faces and an amazingly regular structure.

Among them are the unassuming crystals of rock salt—natural sodium chloride, i.e. common salt. They are found in nature in the form of rectangular parallelepipeds or cubes. Calcite crystals also have a simple form—transparent oblique-angled parallelepipeds. Quartz crystals are much more complicated. Each little crystal has a great many faces of different shapes, intersecting in edges of different lengths.

However, a crystal is anything but a museum-piece. Crystals surround us everywhere. The solid bodies with which we build homes and make machines, the substances which we use in our daily lives almost all of them are crystals. But why do we not see this? The reason is that in nature we rarely come across bodies in the form of single individual crystals (or, as is said, monocrystals). Substances are most often found in the form of firmly linked crystalline grains of very small size, less than a thousandth of a millimetre. Such a structure can only be seen through a microscope.

Bodies consisting of tiny crystalline grains are called polycrystalline (derived from the Greek *polys* meaning "many").

Of course, polycrystalline bodies must also be included among the crystals. It will then turn out that almost all the solid bodies surrounding us are crystals. Sand and granite, copper and iron, the salol sold in a drug store and paint all these are crystals.

There are exceptions; glass and plastics do not consist of small crystals. Such solid bodies are called amorphous.

Thus, studying crystals means studying almost all the bodies surrounding us. It is obvious that this is important.

Single crystals are recognized at once by the regularity of their shapes. Plane faces and straight edges are characteristic properties of a crystal; the regularity of shape is undoubtedly related to the regularity of the internal structure of a crystal. If a crystal has been especially stretched in a certain direction, it means that the structure of the crystal in this direction is also special in some way.

But imagine that a ball has been made by machine out of a large crystal. Will we succeed in figuring out that we have a crystal in our hands, in distinguishing this ball from a glass ball? Since the different faces of a crystal are developed to different degrees, this suggests that the physical properties of a crystal also differ in different directions. This, of course, refers to the strength of a crystal, its electrical conductivity and to many other properties. This peculiarity of a crystal is called the anisotropy of its properties. Anisotropic means different properties in different directions.

Crystals are anisotropic. On the contrary, amorphous bodies, liquids and gases are isotropic, i.e. possess identical (derived from the Greek *isos* meaning "equal") properties in different directions (derived from the Greek *tropos* meaning "turning"). The anisotropy of the properties of a crystal is precisely what permits us to find out whether or not a transparent, formless piece of matter is a crystal.

Let us visit a mineralogical museum and closely examine various monocrystalline specimens of crystals of the same substance. It is quite possible that specimens of both regular and irregular shapes are on display. Some of the crystals resemble fragments, others have one or two abnormally developed faces.

From the collection of specimens we select the ones that seem to be of perfect shape and sketch them. The drawing we obtain is shown in Figure 2.6. Quartz has again been taken as an example. As the crystals of other substances, quartz can develop a different number of faces of each "kind", as well as a different number of "kinds" of faces. Even if their similarity in appearance is not

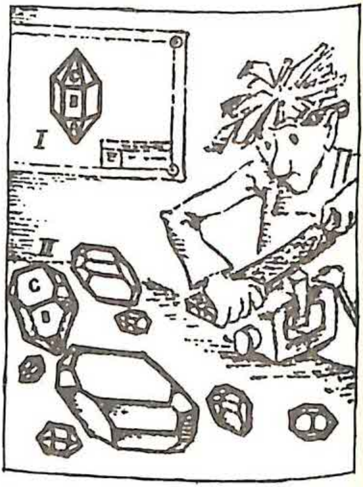

Figure 2.6

self-evident, such small crystals do resemble one another as do close relatives or, sometimes, as twins. In what does their similarity consist?

Look carefully at Figure 2.6, which illustrates a number of quartz crystals. All of them are close "relatives". They can be made truly similar by grinding off various faces by different amounts in such a way that they remain parallel to their initial positions. It is readily evident, for instance, that crystal *II* can be made, in this way, entirely similar to crystal *I*. This is possible because the angles are equal between like faces, for example, between faces *A* and *B*, *B* and *C*, etc.

It is this equality of angles that gives the crystals their "family" resemblance. As the faces are ground off parallel to their initial positions, the shape of the crystal is changed, but the angles between the faces are retained.
]

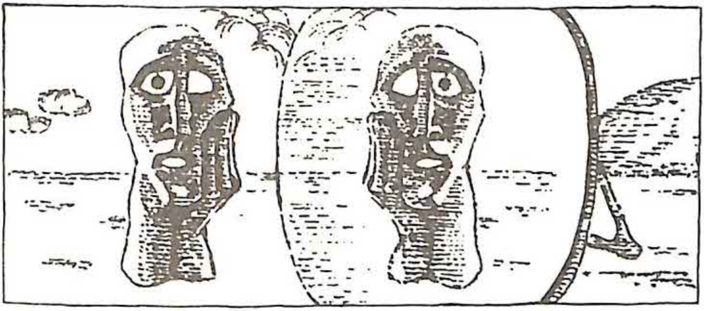

Figure 2.7

As a crystal grows, certain of its faces, due to various random factors, may be in more favourable, and others in less favourable conditions for the addition of new layers of atoms or molecules. Crystals grown under different conditions may not appreciably resemble one another, as far as their appearance is concerned, but the angles between the corresponding faces of all crystals of the substance being considered are always the same. The shape (or *habit*, as it is called) of a crystal is a matter of chance, but the angles between its faces (and you will understand why further on) depend upon its internal structure.

The flatness of its faces is not the only feature that distinguishes a crystal from shapeless bodies. A crystal also possesses symmetry. The meaning of this word, in the sense we are about to employ, can best be demonstrated by examples.

Illustrated in Figure 2.7 is a statue (reminding us of the famous ones on Easter Island) standing in front of a large mirror. The reflection in the mirror is an exact copy (actually a mirror image) of the statue. The sculptor could have carved two statues and arranged them in the same manner as our statue and its reflection in the mirror.

This double sculpture is a symmetrical figure; it consists of two equal parts, one being a mirror image of the other and equal in the sense that one's left hand is equivalent to one's right.

Let us assume that a flat mirror is placed as in Figure 2.7. Then the right-hand part of the sculpture exactly coincides with the reflection of its left-hand part. Such a symmetrical arrangement would have a vertical plane of mirror symmetry passing through the centre between the two parts. The plane of symmetry is an imaginary one, but we sense it distinctly in examining a symmetrical body.

The bodies of animals have planes of symmetry; a vertical plane of external symmetry can be passed through a man as well. Symmetry is only approximate in the animal world, and, in general, there is no ideal symmetry in the world around us. An architector can design a house consisting of two ideally symmetrical halves. But when the house is built, no matter how well, you can always find some difference in the two symmetrical parts: one may have a crack at some place where the other has not.

The most exact symmetry is found in the world of crystals, though it is hardly ideal here either. Fissures invisible to the naked eye, scratches and other flaws always make equal faces differ slightly from one another.

The child's toy called a pinwheel is illustrated in Figure 2.8. It is also symmetrical, but you cannot pass a plane of symmetry through it in any way. What then is symmetrical about this toy? First, let us consider its symmetrical parts. How many are there? Obviously, four. What makes their mutual arrangement regular? This, too, is simple enough. Let us turn the pinwheel counterclockwise through a right angle, i.e. one-fourth of a revolution. Now vane *1* has turned to the previous position of vane *2*, *2* to that of vane *3*, *3* to that of vane *4*,

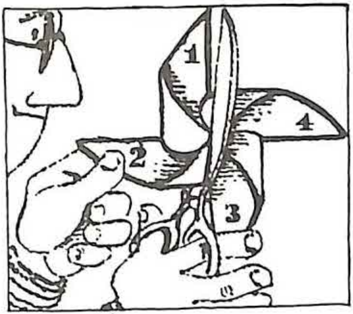

Figure 2.8

and *4* to that of vane *1*. The new position of the pinwheel cannot be distinguished from the previous one. We say that such a figure has an axis of symmetry or, more precisely, an axis of four-fold symmetry because it coincides with itself after turning through one-fourth of a revolution.

Thus, an axis of rotation symmetry is an imaginary straight line about which a body, when turned through a unit fraction of a revolution, is in a position that cannot be distinguished from its initial position. The order of rotation symmetry (four-fold in our case) indicates that such coincidence occurs after turning the body one-fourth of a revolution. Consequently, after four such turning motions we return to the initial position.

Do we find symmetry of all kinds in the crystal kingdom? Investigations have shown that we do not. In fact, the only axes of rotation symmetry found in crystals are the two-, three-, four- and six-fold ones. This is no mere chance. Crystallographers have shown that it is related with the internal structure of crystals. Therefore, the number of different kinds or, as we say, classes of crystal symmetry is relatively small—only 32.

Structure of Crystals

Why is the regular shape of a crystal so beautiful? Its faces, so smooth and shining, look as though they were polished by a skilled lapidary. Different parts of the crystal repeat one another, forming a handsome symmetrical figure. This exceptional regularity of crystals has been known since time immemorial. But the concepts of the ancient scholars on the nature of crystals differed only slightly from the tales and legends made up by poets whose imagination was fascinated by the beauty and elegance of crystals. It was believed that rock crystal is formed of ice, and diamond of rock crystal. Many wonderous properties were attributed to crystals; they were thought to heal diseases, protect one against poisons, have an influence on one's fate and many others.

The first scientific views on the nature of crystals appeared only in the 17th and 18th centuries. An idea of these conceptions is given by Figure 2.9, which was reproduced from *Traitė de Mineralogie*, written by the French abbé, René Just Haüy, near the end of the 18th century. According to its author, crystals are made up of tiny "building blocks", fitting tightly to one another. This conclusion is one that is naturally arrived at. Let us break up a crystal of Iceland spar (calcite, or calcium carbonate) with a sharp blow of a hammer. It flies apart into pieces of various sizes. Examining them carefully, we find that the pieces are of regular shape, quite similar to that of the large crystal, their "parent". Evidently, reasoned Haüy, if we continue to break up the pieces into smaller and smaller ones, we will finally reach the smallest building block, invisible to the naked eye, which is a crystal of the given substance. These ultimate blocks are so small that steps formed by them, comprising the faces of the large crystal, seem to us to be immaculate-

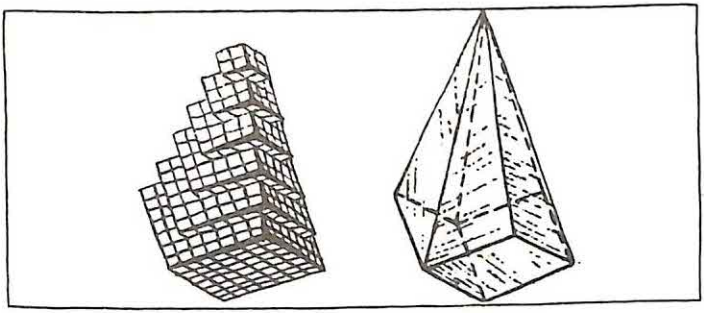

Figure 2.9

ly smooth. Well, and what is this final building block like? The scientists of that day could not answer this question.

The "building block" theory of crystal structure was of great benefit to science. It explained the origin of the straight edges and flat faces of a crystal. As a crystal grows, new building blocks attach themselves to those of the crystal, and a face grows like the wall of a house built by the hands of bricklayers.

Hence, the question concerning the reason for the regularity and beauty of the shapes of crystals has been answered a long time ago. The reason for this phenomenon is their internal regularity. This regularity consists in the endless repetition of one and the same elementary parts.

Imagine a park fence made of rods of different lengths and distributed helter-skelter. An ugly scene. A good fence is constructed from identical rods distributed in a regular sequence at equal distances from each other. We find such a self-repeating pattern on wallpaper. Here an element of a drawing, say, a girl playing with a ball, is repeated not only in one direction, as in a park fence, but so that it fills a plane.

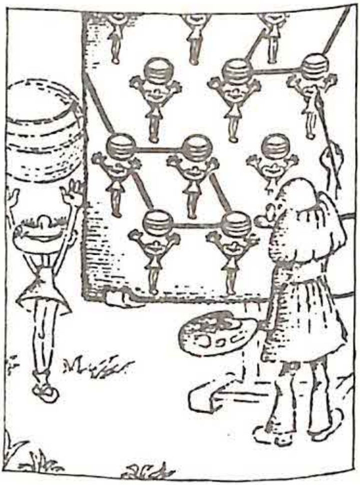

Figure 2.10

But what relationship do a park fence and wallpaper have to a crystal? A most direct one. A park fence consists of links repeating along a line, wallpaper of patterns repeating in a plane, and a crystal of groups of atoms repeating in space. One therefore says that the atoms of a crystal form a space (or crystal) lattice.

There are certain details concerning a three-dimensional, or space, lattice that we must now discuss. To simplify the work of the illustrator, we shall explain all that is required, using wallpaper as an example, rather than asking him to construct complicated drawings of three-dimensional figures.

Separated out in Figure 2.10 is the smallest piece that can be transferred or shifted to obtain the whole pattern of the wallpaper. To separate out such a piece, we draw two straight lines from any point of the drawing, for instance, the centre of the beach ball, connecting it to the same points of the two adjacent balls. As can be seen in our drawing, we can use these two lines to construct a parallelogram. By shifting or transferring this parallelogram along the directions of the two initial basic lines over distances equal to its sides, we can obtain the whole wallpaper pattern. This smallest repeated portion, commonly called a unit cell, can be selected in various ways. It is evident from Figure 2.10 that several different parallelograms could be selected, each containing one drawing. We emphasize that in the given case it makes no difference to us whether the picture inside the cell is a whole one or it is divided up by the lines bounding the cell.

It would be a mistake to suppose that after drawing the repeating picture, called the motif, for the wallpaper the artist can always consider his job to be finished. This would be true if the only way to make a pattern for wallpaper was to add to the given portion another identical portion, shifted parallel to the first along the two initial basic lines.

In addition to this simplest method, however, there are sixteen more ways to fill in the wallpaper design with an orderly repeated drawing, or motif, i.e. seventeen types of mutual arrangement of drawings on a plane. They are illustrated in Figure 2.11. Here a simpler repeating motif has been selected, but, like the one in Figure 2.10, it has no symmetry in itself. The patterns composed of this motif are symmetrical and the difference in the patterns is due to the difference in the symmetrical arrangements of the motifs.

We see, for example, that in the first three cases the pattern has no plane of mirror symmetry: you cannot position a vertical mirror so that one part of the pattern is a mirror reflection of another part. Cases 4 and 5, on the contrary, have planes of symmetry. Two mutually perpendicular mirrors can be set up in cases 8 and 9,

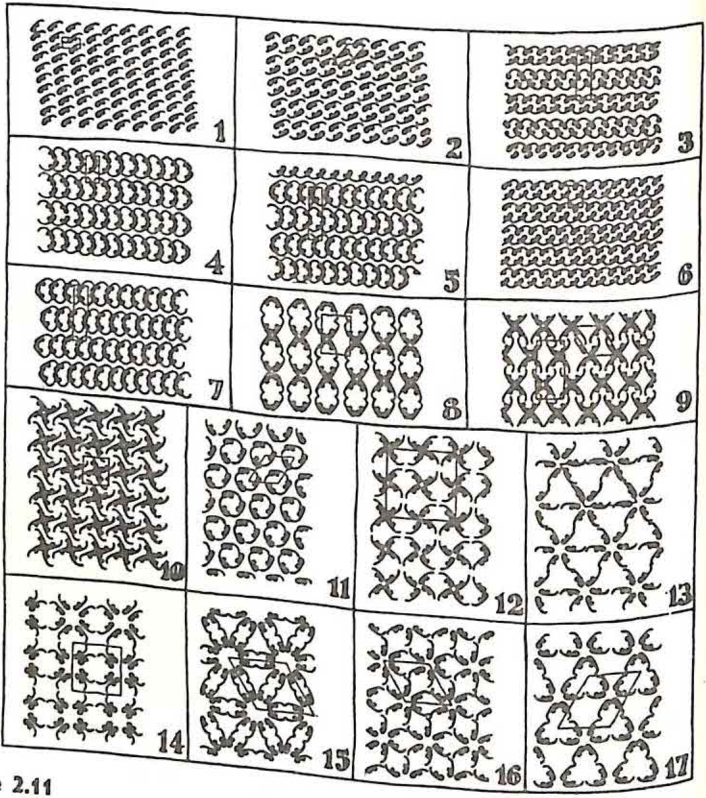

Figure 2.11

Case 10 has an axis of four-fold rotation symmetry, perpendicular to the plane of the drawing. In case 11, the axis is of three-fold symmetry, and in cases 13 and 15, of six-fold rotation symmetry.

Planes and axes of symmetry are found on our drawings in parallel series or families, rather than singly. If you have found one point through which you can pass an

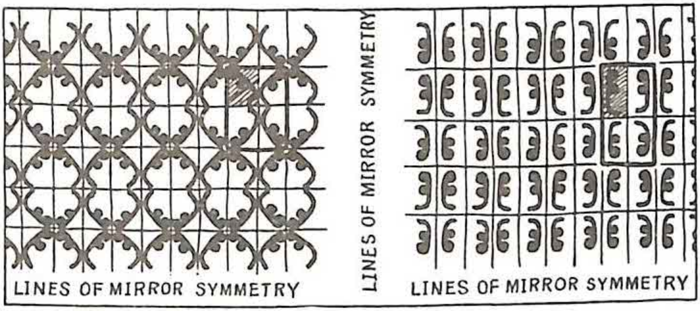

Figure 2.12

axis (or plane) of symmetry, you can readily find the adjacent point and consecutive points, all spaced at the same distance from one another, through which the same kind of axes (or planes) of symmetry can be passed.

The seventeen types of symmetry of a plane pattern do not, of course, exhaust all of the great variety of patterns that can be composed from a single motif. The artist must specify one more condition: how the motif is to be positioned with respect to the boundary lines of the cell. Figure 2.12 illustrates two wallpaper patterns with the same initial motif which is differently positioned in each pattern with respect to the lines representing the vertical mirrors (in a plane pattern they are simply lines of symmetry). Both patterns come under case 8 in Figure 2.11.

Each body, including crystals, consists of atoms. Simple substances, or elements, consist of atoms of a single kind. Complex substances, or compounds, consist of atoms of two or several kinds. Assume that in some superpowerful microscope we could examine the surface of a crystal of common salt and see the centres of the atoms. Figure 2.13 shows how we would see the

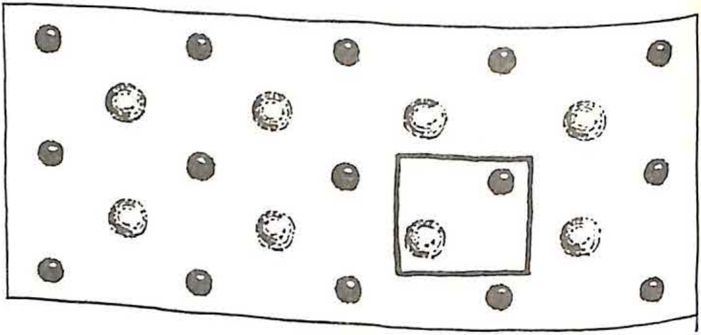

Figure 2.13

atoms arranged along a face of the crystal like a wallpaper pattern. You can readily understand now how a crystal is constructed. We could say that a crystal resembles "three-dimensional wallpaper". A crystal is composed by joining three-dimensional unit cells tightly together instead of plane cells as for wallpaper patterns. These three-dimensional unit cells are the building blocks of which the crystals are built.

How many different ways exist for building up three-dimensional wallpaper patterns from these elementary pieces? This complex mathematical problem was solved at the turn of the century by the founder of structural crystallography Yevgraf Stepanovich Fedorov (1853-1919). This eminent Russian scientist established the fact that there can be only 230 different ways to build up a crystal or, as they say today, 230 Fedorov groups.

All that is known today about the internal structure of crystals was obtained by X-ray structure analysis, which we shall describe in some detail in the fourth book.

Simple crystals exist, made up of atoms of a single kind. Diamond, for example, is of pure carbon. Crystals of common salt consist of ions (electrically charged atoms) of two kinds: sodium and chlorine. More complex crystals may be made up of molecules which, in their turn, consist of atoms of many kinds.

We can always single out in a crystal the smallest repeating groups of atoms (or single atoms, in the simplest case). Such a group is called the unit cell.

The dimensions of unit cells may vary in wide ranges. The shortest distances are found between the adjacent lattice points (corners of the unit cell) of the simplest crystals, consisting of atoms of a single kind. The maximum distances are found in complex protein crystals. These distances, called lattice constants, range from 2 or 3 angstroms to several hundred angstroms (hundredths of one-millionth of a centimetre).

There are a great variety of crystal lattices. The properties common to all crystals are due to their lattice structure. To begin with, we can readily understand that the ideally flat faces of a crystal are the planes passing through the lattice points at which atoms are located. But any number of lattice planes can be passed in the most diverse directions. Which of these planes bound the grown crystals, i.e. become its faces?

Let us turn our attention, first of all, to the following circumstance: various lattice planes and lines are not filled equally densely with lattice points. Experiments show that a crystal is faceted by the planes that are most densely studded with lattice points and that these planes intersect at edges which are also most densely occupied by lattice points.

A view of a crystal lattice perpendicular to a face is shown in Figure 2.14. Shown also are the traces of lattice planes perpendicular to the drawing. It should be clear from what has been said that faces on the crystal parallel to planes *I* and *III* are apt to develop. No faces will be developed parallel to plane *II* which is so sparsely dotted with lattice points (and atoms).

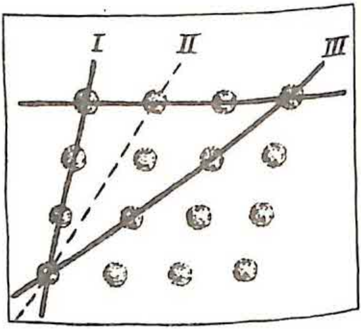

Figure 2.14

The structures of many hundreds of crystals are known today. We shall discuss the structures of the simplest crystals, first of all, those built up of atoms of a single kind.

Three types of lattices are most common. They are shown in Figure 2.15. The centres of the atoms are represented by points; the lines joining the points do not have any actual meaning. They have been drawn merely to make the nature of the spatial distribution of the atoms clearer to the reader

Figures 2.15*a* and *b* depict cubic lattices. In order to visualize these lattices more clearly, imagine that you have arranged building blocks in the simplest manner—edge to edge and face to face. If you now conceptually place points at the vertices and centres of the cubes, the cubic lattice depicted in Figure 2.15*a* appears. Such a structure is called body-centred cubic. If points are placed at the vertices of the cubes and at the centres of their faces, the cubic lattice depicted in Figure 2.15*b* appears. It is called face-centred cubic.

The third lattice (Figure 2.15*c*) is called close-packed hexagonal (i.e. having six angles). In order to understand the origin of this term and more clearly visualize the dis-

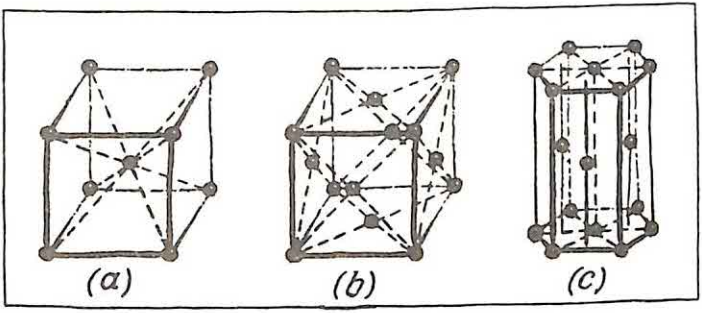

Figure 2.15

tribution of the atoms in this lattice, let us take some billiard balls and start packing them as closely as possible. First of all, let us form a close layer—it looks like billiard balls which have been gathered in by a rack before the beginning of a game (Figure 2.16). Note that the ball in the middle of the triangle is in contact with six neighbours, and these six neighbours form a hexagon. We continue the packing by laying one layer upon another. If we place the balls of the second layer directly above the balls of the first, such a packing would not be close. Trying to distribute the greatest number of balls in a definite volume, we should place the balls of the second layer in the holes formed by the first, the balls of the third layer in the holes of the second, etc. In a close-packed hexagonal lattice, the balls of the third layer are placed in such a way that their centres lie directly above those of the balls of the first.

The centres of the atoms in a close-packed hexagonal lattice are distributed just like those of the balls which are closely packed in the manner described.

A great many elements crystallize in the lattices of the three types described above:

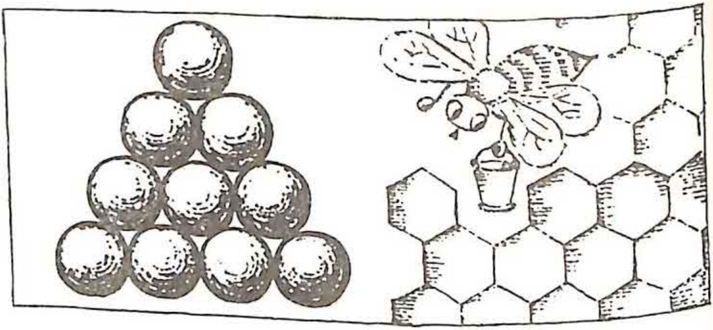

Figure 2.16

Close-packed hexagonal lattice	Be, Co, Hf, Ti, Zn, Zr
Face-centred cubic	Al, Cu, Co, Fe, Au, Ge, Ni, Ti
Body-centred cubic	Cr, Fe, Li, Mo, Ta, Ti, U, V

We shall mention only a few of the other structures. The structure of diamond is depicted in Figure 2.17. What is characteristic of this structure is that a carbon atom in diamond has four immediate neighbours. Let us compare this number with the corresponding numbers for the three most common structures just described. As is evident from the figures, each atom has 12 immediate neighbours in a close-packed hexagonal lattice, the atoms forming a face-centred cubic lattice have just as many neighbours, and each atom has eight neighbours in a body-centred lattice.

We shall say a few words about graphite, whose structure is shown in Figure 2.18. This structure has a striking peculiarity. Graphite consists of layers of atoms, where atoms of a single layer are more firmly bound to each other than atoms of neighbouring layers. This is related to the values of the interatomic distances: the distance between neighbours in a single layer is 2.5 times as small as the shortest distance between layers.

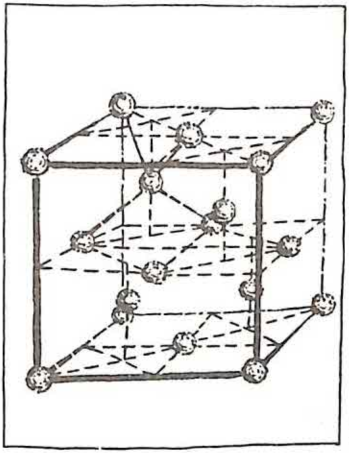

Figure 2.17

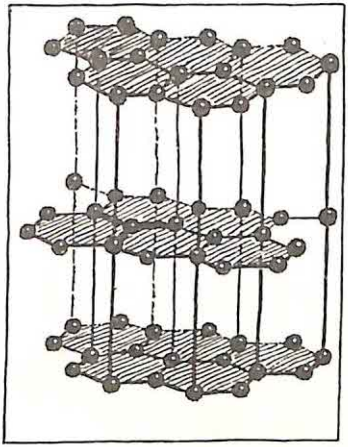

Figure 2.18

The presence of weakly bound atomic layers makes it easy for graphite crystals to break up along these layers. This is why solid graphite can serve as a lubricant in those cases when it is impossible to apply lubricating oil—for example, at very low or very high temperatures. Graphite is a solid lubricant.

Friction between two bodies reduces, roughly speaking, to the fact that microscopic protuberances of one body fall in hollows of the other. The force required for breaking up a microscopic graphite crystal is much smaller than the frictional forces; therefore, a graphite lubrication considerably facilitates the sliding of one body along another.

There is an endless variety in the structures of crystals of chemical compounds. The structures of rock salt and carbon dioxide depicted in Figures 2.19 and 2.20 can serve as extreme examples.

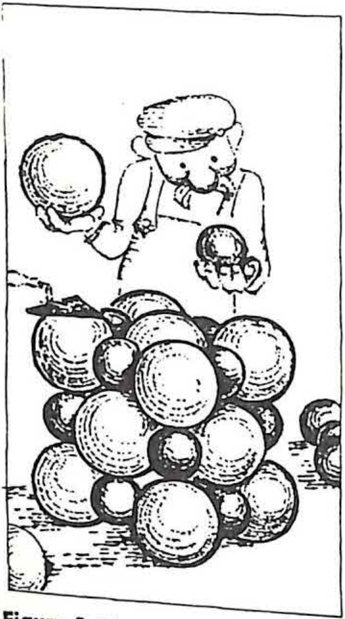

Figure 2.19

Figure 2.20

Crystals of rock salt (Figure 2.19) consist of atoms of sodium (small dark balls) and chlorine (large light balls) alternating along the axes of a cube. Each sodium atom has six equidistant neighbours of the other kind. The same is also true of chlorine. But where are the molecules of sodium chloride? There are none; not only are groups of single atoms of sodium and single atoms of chlorine absent from salt crystals, but in general, no group of atoms whatsoever can be distinguished from the others by their proximity.

The chemical formula of NaCl does not give us any grounds for saying that "this substance is built up out of molecules of NaCl". The chemical formula merely

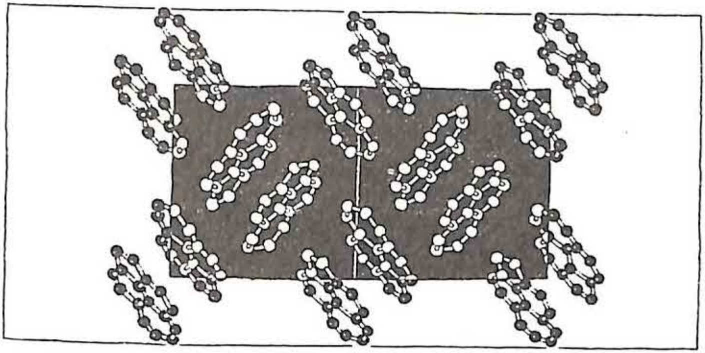

Figure 2.21

indicates that the substance is constructed from the same number of atoms of sodium and chlorine.

The question of the existence of molecules in a substance is decided by its structure. If no groups of close atoms can be distinguished in it, there are no molecules.

A crystal of carbon dioxide, CO_2 (the dry ice which lies in cartons of ice cream), is an example of a molecular crystal (Figure 2.20).

The centres of the oxygen and carbon atoms of a molecule of CO_2 are situated along a straight line (see Figure 2.2). The distance C—O is equal to 1.3 Å, and the distance between oxygen atoms of neighbouring molecules is about 3 Å. It is obvious that under such conditions we immediately "recognize" a molecule in a crystal.

Molecular crystals are close packings of molecules. In order to see this, we must outline the contours of the molecules. This is precisely what has been done in Figure 2.20.

All organic substances consist of molecular crystals. Organic molecules frequently consist of many tens and even hundreds of atoms (those made up of tens of thousands of atoms are to be discussed in a separate chapter). It is impossible to properly depict their packing arrangements graphically. For this reason, you may find drawings similar to Figure 2.21 in books in this field. The molecules of this organic substance are built up of carbon atoms. The bars between the atoms represent the valence bonds. The molecules seem to be suspended in air. But do not believe what you see here. They have been drawn thus to give you an idea of how the molecules are arranged in a crystal. For the sake of simplicity, the illustrator did not show the hydrogen atoms joined to the outer atoms of carbon (as a matter of fact, chemists frequently make their similar omissions). He did not even consider it necessary to outline the molecule, imparting a definite shape to it. If he had, we would see that the principle of molecular packing, with the "key fitting the lock", is just as valid in this case as in other similar ones.

Polycrystalline Substances

We have already mentioned the fact that amorphous bodies are rare in the world of solids. Most of the objects surrounding us consist of tiny crystalline grains, about a thousandth of a millimetre in size.

Investigators discovered the granular structure of metals in the 19th century with the aid of ordinary optical microscopes. All that was required was an arrangement enabling the specimens to be observed in reflected instead of transmitted light. Up-to-date metallurgical microscopes operate on this same principle.

The image seen in such a microscope may be like that shown in Figure 2.22. The grain boundaries are usually quite distinct. As a rule, impurities accumulate at the boundaries.

The properties of materials depend to an exceptionally large degree on the size of the grains, their orientation

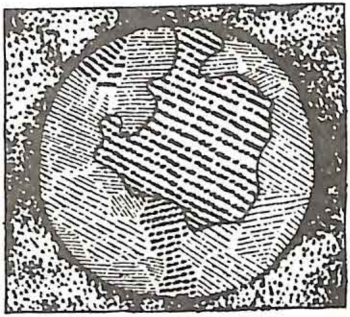

Figure 2.22

and what is happening at their boundaries. For this reason, physicists have devoted much research to the study of polycrystalline substances. By means of X-ray structure analysis, about which we have already promised to tell our readers, they found that each grain is a small crystal. We repeat our promise.

All treatment of a metal affects its grains. Suppose we have a piece of cast metal. Its grains are in disorder and their size is quite large. Then we make wire of the piece of metal by drawing it through a die. What happens to the crystalline grains in this plastic working operation? Investigations have shown that the change in shape of a solid in drawing wire or in some other plastic working technique breaks up the crystalline grains. At the same time, a certain element of order is produced in the arrangement of these grains by the action of the mechanical forces. But what possible kind of order can there be here? The fragments of the grains are absolutely shapeless.

This is true: the fragments may be of any random shape, but a fragment of a crystal is still a crystal and the atoms in its lattice are packed as regularly as in any well-faceted crystal. Hence, we can indicate in each fragment how its unit cells are oriented. Prior to plastic working,

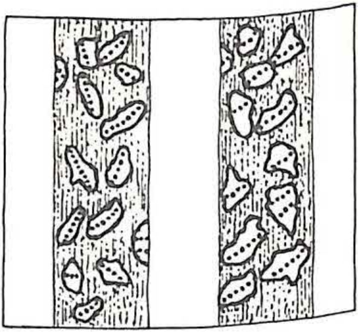

Figure 2.23

the cells are strictly ordered only within each separate grain; there is, as a rule, no total order. After the metal is worked, the grains align themselves so that a certain general order becomes evident in their cells. This is called *texture*. For example, the diagonals of the cells in all the grains become oriented approximately parallel to the direction in which the metal is worked.

Texture is illustrated in Figure 2.23 (at the right) by the example of certain definite, indicated planes in the grains. These planes are most densely filled with atoms and are shown by rows of dots. The illustration at the left shows the grains of the metal before being worked.

The various kinds of plastic working operations (rolling, forging, and wire-drawing) produce textures of different types. In some operations, the grains turn so that the diagonals of their unit cells are aligned along the direction of working, while in others the edges of the cells are aligned, etc. The more advanced the rolling or wire-drawing technique, the more perfect the texture of the crystalline grains of metal. Texture has a striking effect on the mechanical properties of metal articles. A study of the arrangement and size of the crystalline grains in metals led to an understanding of the fundamental principles involved in the plastic working of metals. This, in turn, led to the improvements of the techniques employed.

Another important kind of metal treatment, annealing, is also associated with the rearrangement of the metal grains. If rolled or drawn metal is heated to a sufficiently high temperature, new crystals are formed, which grow at the expense of the old ones. Annealing gradually destroys the texture; the new crystals are arranged disorderly. As the temperature is raised (or the metal is held longer at the annealing temperature), new grains grow and the old ones disappear. The grains can grow to a size visible to the naked eye. Annealing drastically alters the properties of a metal. It becomes more ductile and softer. This occurs because the grains become coarser and the texture disappears.

3. Temperature

Thermometer

If two differently heated bodies are brought into contact, the warmer one will cool off and the colder one will warm up. It is said that two such bodies exchange heat.

As we have already said, heat exchange is a kind of energy transfer; the body which gives off energy is said to be hotter. We feel that a body is hot if it makes our hand warm, transfers energy to it. On the contrary. if a body is felt to be cold, this means that it is taking energy away from our body.

Concerning a body which is giving off heat (i.e. giving off energy by means of heat exchange), we say: its temperature is higher than that of the body which is taking in this heat.

Observing whether an object of interest to us is cooling off or warming up in the presence of one or another body, we find "its place" in a row of heated bodies. Temperature is a kind of mark indicating for which bodies the object of interest to us will be a giver, and for which a receiver, of heat.

Temperature is measured by thermometers.

The structure of thermometers can be based on the utilization of various properties of bodies sensitive to temperature. The most frequently utilized property is the expansion of bodies during a rise in temperature.

If the body of a thermometer changes its volume when in contact with various bodies, this implies that these bodies have different temperatures. When the volume of the body of a thermometer is greater, the temperature is higher, and when the volume is smaller, the temperature is lower.

There are various substances that can serve as thermometers: liquids (such as mercury or alcohol), solids (such as metals), and gases. But different substances expand differently, and so mercurial, alcoholic, gaseous and other "degrees" will not coincide. Of course, two basic points, the melting point of ice and the boiling point of water, can always be marked on all thermometers. Therefore, all thermometers will indicate 0 and 100 degrees centigrade identically. But bodies will not expand identically between 0 and 100 degrees. One body expands rapidly between 0 and 50 degrees on a mercury thermometer, and slowly in the second part of this interval, but another, vice versa.

Having made thermometers with differently expanding bodies, we will discover noticeable discrepancies in their readings, in spite of the fact that their readings will coincide for the basic points. Moreover, a water thermometer would lead us to the following discovery: if a body cooled to zero is placed on an electric stove, its "water temperature" would first fall and then rise. This happens because water at first decreases its volume when heated, and only later behaves "normally", i.e. increases its volume when heated.

We see that a rash choice of material for a thermometer can bring us to an impasse.

But then what should we be guided by in choosing a "true" thermometer? Which body would be ideal for this purpose?

We have already spoken about such ideal bodies. They are ideal gases. There are no interactions between the particles of an ideal gas and, studying the expansion of an ideal gas, we study how the motion of its molecules changes. This is precisely the reason why an ideal gas is an ideal body for a thermometer.

And it really is a striking fact that while water does not expand like alcohol (nor alcohol like glass, nor glass like iron), then hydrogen, oxygen, nitrogen and any other gas in a sufficiently rarefied state to deserve being called ideal expand in exactly the same fashion when heated.

Therefore, the changes in volume undergone by a definite amount of ideal gas serve as the basis for defining temperature in physics. Of course, in view of the fact that gases are highly compressible, one must be especially careful in seeing to it that the gas is under constant pressure.

In order to graduate a gas thermometer, we should accurately measure the volume of the gas we have chosen at 0° and at 100 °C. We shall divide the difference between the volumes V_{100} and V_0 into 100 equal parts. In other words, the change in the volume of the gas by $(V_{100} - V_0)/100$ corresponds to one degree centigrade (1 °C).

Let us now suppose that our thermometer shows a volume V. What temperature t °C corresponds to this volume? It is not difficult to comprehend that

$$t\,^{\circ}\mathrm{C} = \frac{V - V_0}{V_{100} - V_0}\,100, \quad \text{i.e.} \quad \frac{t\,^{\circ}\mathrm{C}}{100} = \frac{V - V_0}{V_{100} - V_0}$$

By means of this equality, we assign each volume V to a temperature t and obtain the temperature scale* which physicists use.

---

*The *centigrade scale* at which 0 °C is taken as the melting point of ice, and 100 °C as the boiling point of water (both at the standard pressure of 760 mm Hg) is very convenient. In spite of this, the British and the Americans have so far been using a temperature scale which seems very strange to us. How, for

With a rise in temperature, the volume of a gas increases without bound—there is no theoretical limit to the growth in temperature. On the contrary, low (negative on the centigrade scale) temperatures have a limit.

What will happen when the temperature is lowered? A real gas will eventually turn into a liquid, and with an even greater fall in temperature, will solidify. The gas molecules will gather in a small volume. But what will this volume be equal to for a thermometer filled with an ideal gas? Its molecules do not interact with each other and do not have any volume of their own. Hence, a decrease in temperature brings an ideal gas to a zero volume. It is quite possible to come as close as we wish in practice to a behaviour that is characteristic of an ideal gas, for example, to a zero volume. For this it is necessary to fill up the gas thermometer with more and more rarefied gas. Therefore, we won't go wrong by assuming the minimum volume of the gas equal to zero.

According to our formula, the lowest possible temperature corresponds to a zero volume. This temperature is called the *absolute zero* of temperature.

---

example, will you react to the following sentence taken from an English novel: "The summer wasn't hot, the temperature was 60-70 degrees." A misprint? No, the Fahrenheit scale (°F). The temperature in England rarely falls below −20 °C. Fahrenheit selected a mixture of ice and salt having approximately such a temperature and took this temperature for his zero. In the words of the inventor, the standard temperature of a human body was taken for 100° on this scale. However, in order to determine this point, Fahrenheit probably made use of the services of a slightly feverish person. On the *Fahrenheit scale*, the average standard temperature of a human body is 98 °F. On this scale, water freezes at +32 °F and boils at 212 °F. The conversion formula will be:

$$t\,^\circ\mathrm{C}=\frac{5}{9}(t-32)\,^\circ\mathrm{F}$$

In order to determine the position of absolute zero on the centigrade scale, we must substitute zero for the volume ($V = 0$) in the temperature formula just derived. Consequently, the temperature of absolute zero is equal to $-100V_0/(V_{100} - V_0)$.

It turns out that this remarkable point corresponds to a temperature of about −273 °C (more precisely, −273.15 °C).

Thus, there are no temperatures below absolute zero; for they would correspond to negative volumes of a gas. It doesn't make sense to speak of lower temperatures. It is just as impossible to obtain temperatures below absolute zero as to make a wire with a diameter less than zero.

It is impossible to cool a body at absolute zero, i.e. one cannot take energy away from it. In other words, bodies and the particles they are made of have the least possible energy at absolute zero. This implies that the kinetic energy equals zero and the potential energy assumes its least possible value at absolute zero.

Since absolute zero is the lowest temperature, it is only natural that the *absolute scale* in which readings begin at absolute zero be used in physics, especially in those of its branches where low temperatures play an important role. It is clear that $T_{\text{abs}} = (t + 273)$ °C. Room temperature will be about 300 °C on the absolute scale. The absolute scale is also called the *Kelvin scale*, in honour of the well-known 19th century English scientist, and the notation T K is employed in place of T_{abs}.

A formula for a gas thermometer determining the absolute temperature T can be written down in the form

$$T = 100\frac{V - V_0}{V_{100} - V_0} + 273$$

Using the equality $100V_0/(V_{100} - V_0) = 273$, we arrive at the following simple result:

$$\frac{T}{273} = \frac{V}{V_0}$$

Therefore, the absolute temperature is simply proportional to the volume of an ideal gas.

Exact measurements of temperature require all kinds of contrivances on the part of the physicist. Mercury, alcohol (for Arctic regions) and other thermometers are graduated by comparison with a gas thermometer over a rather wide temperature interval. However, it too is also unsuitable for temperatures very close to absolute zero (below 0.7 K), when all gases liquefy, and also for temperatures above 600 °C, when gases penetrate glass. Other principles of temperature measurement are used for high and very low temperatures.

As for practical methods of measuring temperature, they are manifold. Instruments based on electrical phenomena are of great significance. It is now important to remember only one thing—during all measurements of temperature, we should be convinced that the reading obtained completely coincides with what a measurement of the expansion of a rarefied gas would give.

High temperatures arise in ovens, furnaces and burners. Temperatures of 220-280 °C are attained in baking ovens. Higher temperatures are applied in metallurgy—hardening furnaces yield 900-1000 °C, forges yield 1400-1500 °C. Temperatures of 2000 °C are attained in steel furnaces.

The records for high temperature in a furnace are obtained with the aid of electric arcs (about 5000 °C). The arc flame makes it possible "to deal" with the most refractory metals.

And what is the temperature of the flame of a gas burner? The temperature in the inner bluish cone of flame is only 300 °C. The temperature in the outer cone attains 1800 °C.

Incomparably higher temperatures arise during the explosion of an atomic bomb. Judging by indirect estimates, the temperature at the centre of the explosion attains several million degrees.

Attempts have recently been made to obtain such ultrahigh temperatures in special laboratory installations built in the Soviet Union and in other countries. It has proved possible to attain temperatures up to several million degrees for very brief moments.

Ultrahigh temperatures also exist in nature, not on the Earth, but on other bodies in the Universe. In the centres of stars, the Sun in particular, the temperature attains tens of millions of degrees. But the surfaces of stars have a considerably lower temperature, not exceeding 20 000 °C. The surface of the Sun gets heated up to 6000 °C.

Ideal Gas Theory

The properties of an ideal gas, giving us the definition of temperature, are very simple. The Boyle law is valid for constant temperatures: during changes in volume or pressure, the product pV remains constant. For a constant pressure, the quotient V/T is conserved, no matter how the volume or temperature changes. It is easy to unite these two laws. It is clear that the expression pV/T remains the same as for a constant temperature but with changing V and p; the same is true for a constant pressure but with changing V and T. The expression pV/T remains constant during a change not only in any pair, but also simultaneously in all three of the quantities p, V and T. The law $pV/T = \text{const}$ is known as the *equation of state of an ideal gas*.

An ideal gas is chosen for a thermometer because its properties depend only on the motion (but not on the interaction) of its molecules.

What is the nature of the relationship between the motion of molecules and temperature? To answer this question, it is necessary to find the relationship between the pressure of a gas and the motion of the molecules in it.

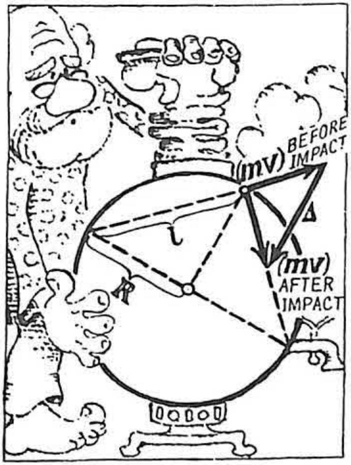

Figure 3.1

In a spherical vessel of radius R, N molecules of a gas are contained (Figure 3.1). Let us follow an arbitrary molecule, for example, one which is moving at a given moment from left to right along a chord of length l. We shall not pay attention to molecular collisions: such impacts do not affect the pressure. Having flown to the boundary of the vessel, the molecule will strike against the wall and fly off in some other direction with the same speed (the collision is elastic). Ideally, such a journey through the vessel might continue eternally. If v is the molecular velocity, each impact will occur after l/v seconds, i.e. each molecule will strike the wall v/l times a second. The continual hail of impacts by the N molecules unites into a single force of pressure.

According to Newton's law, the force is equal to the change in momentum during a unit of time. Let us denote the change in momentum at each impact by Δ. This change occurs v/l times a second. Consequently, the contribution to the force on the part of a single molecule will be $\Delta v/l$.

The momentum vectors before and after an impact, and also the momentum transfer Δ have been constructed in Figure 3.1. It follows from the similarity of the triangles arising in the construction that $\Delta/l = mv/R$. The contribution to the force on the part of a single molecule will take the following form:

$$\frac{mv^2}{R}$$

Since the length of the chord does not occur in the formula, it is clear that molecules moving along arbitrary chords make an identical contribution to the force. Of course, the change in momentum will be smaller for an oblique impact, but then the impacts in this case will be more frequent. Calculations show that these two effects exactly compensate for each other.

Since there are N molecules in the sphere, the resultant force will be equal to

$$\frac{Nmv_{\text{av}}^2}{R}$$

where v_{av} is the average molecular velocity.

The pressure p of the gas equal to the force divided by the surface area of the sphere, $4\pi R^2$, is

$$p=\frac{Nmv_{\text{av}}^2}{4\pi R^2 R}=\frac{\frac{1}{3}Nmv_{\text{av}}^2}{\frac{4}{3}\pi R^3}=\frac{Nmv_{\text{av}}^2}{3V}$$

where V is the volume of the sphere.

Therefore,

$$pV=\frac{1}{3}Nmv_{\text{av}}^2$$

This equation was first derived by Daniel Bernoulli in 1738*.

It follows from the equation of state of an ideal gas that $pV = \text{const}\cdot T$; we see from the equation just derived that pV is proportional to v_{av}^2. Hence,

$$T \propto v_{\text{av}}^2, \quad \text{or} \quad v_{\text{av}} \propto \sqrt{T}$$

i.e. the average velocity of an ideal gas molecule is proportional to the square root of the absolute temperature.

Avogadro's Law

Assume that a substance is a mixture of different molecules. Isn't there a physical quantity characterizing a motion which would be identical for all these molecules, say, for hydrogen and oxygen, provided their temperatures are identical?

Mechanics yields an answer to this question. It can be proved that the average kinetic energy $mv_{\text{av}}^2/2$ of the translatory motion will be identical for all molecules.

This implies that for a given temperature, the average square of the molecular velocities is inversely proportional to the mass of the particles:

$$v_{\text{av}}^2 \propto \frac{1}{m}, \quad \text{or} \quad v_{\text{av}} \propto \frac{1}{\sqrt{m}}$$

Let us return to the equation $pV = (1/3)\ Nmv_{\text{av}}^2$. Since the quantities mv_{av}^2 are identical for all gases at a given temperature, the number N of molecules contained in a given volume V at a definite pressure p and temperature T is identical for all gases. This remarkable law was first formulated by Amedeo Avogadro (1776-1856).

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*Of Swiss origin, D. Bernoulli worked and lived in Russia; he was a member of the St. Petersburg Academy of Sciences. No less well known is the activity of Johann (Jean) Bernoulli and Jakob (Jacques) Bernoulli. All three were brothers, not namesakes.

But how many molecules are there in 1 cm^3? It turns out that there are 2.7×10^{19} molecules in 1 cm^3 at 0 °C and 760 mm Hg. This is an enormous number. So that you can feel just how great it is, let us give an example. Suppose that gas is flowing out of a 1-cm^3 vessel with such a speed that a million molecules leave each second. It isn't hard to calculate that it will take the vessel a million years to get rid of the gas!

Avogadro's law shows that under a definite pressure and temperature, the ratio of the number of molecules to the volume in which they are contained, N/V, is a quantity that is identical for all gases.

Since the density of a gas $\rho = Nm/V$, the ratio of the densities of gases is equal to that of their molecular masses:

$$\frac{\rho_1}{\rho_2} = \frac{m_1}{m_2}$$

The relative masses of molecules can therefore be determined by simply weighing gaseous substances. Such measurements once played a great role in the development of chemistry. It also follows from Avogadro's law that for a mole of any substance in the state of an ideal gas, $pV = kN_A T$, where k is a universal constant (named after the famous German physicist Ludwig Boltzmann) equal to 1.38×10^{-16} erg/K. The product $R = kN_A$ is called the universal gas constant.

The ideal gas law is often written as

$$pV = \mu RT$$

where μ is the amount of substance expressed in moles. This equation is frequently applied in practice.

Molecular Velocities

Theory shows that for a constant temperature, the average kinetic energy of molecules, $mv_{av}^2/2$, is identical. According to our definition of temperature, this average kinetic energy of the translatory motion of the molecules of a gas is proportional to the absolute temperature.

Combining the ideal gas equation with Bernoulli's equation we obtain

$$\left(\frac{mv^2}{2}\right)_{\text{av}}=\frac{2}{3}kT$$

Temperature measurements with a thermometer filled with an ideal gas add a meaning of rare simplicity to this measure. The temperature is proportional to the average value of the energy of translatory motion of the molecules. Since we live in three-dimensional space, we can say that a point moving at random has three degrees of freedom. Consequently, there is $kT/2$ energy per degree of freedom of a moving particle.

Let us determine the average speed of oxygen molecules at room temperature, which we take to be 27 °C = = 300 K in round numbers. The molecular mass of oxygen is 32, so the mass of one molecule equals $32/(6\times10^{23})$ g. A simple computation yields $v_{\text{av}} = 4.8 \times 10^4$ cm/s, i.e. about 500 m/s. Molecules of hydrogen move considerably faster. Their masses are 16 times as small, and their speeds are $\sqrt{16} = 4$ times as great, i.e. are about 2 km/s at room temperature. Let us estimate the thermal speed of a small particle which is visible through a microscope. An ordinary microscope permits us to see a dust particle of 1 μm (10^{-4} cm) in diameter. The mass of such a particle with a density close to unity will be in the neighbourhood of 5×10^{-13} g. We obtain about 0.5 cm/s for its speed. It is not surprising that such motion is quite noticeable.

The speed of the Brownian movement of a particle with a mass of 0.1 g will be only 10^{-6} cm/s in all. It is no wonder that we do not see the Brownian movement of such particles.

We have spoken of the average speed of a molecule. But not all molecules move with the same speed; a cer-

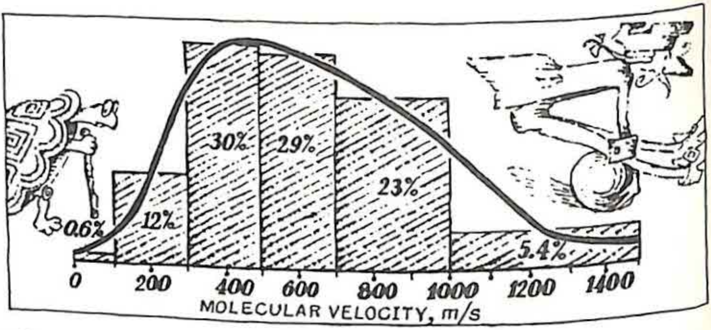

Figure 3.2

tain fraction of the molecules move faster, but others move slower. It turns out that this can all be calculated. We shall only present the results.

At a temperature of about 15 °C, for example, the average speed of nitrogen molecules is equal to 500 m/s; 59% of the molecules move with speeds between 300 and 700 m/s. Only 0.6% of the molecules move with small speeds—from 0 to 100 m/s. There are only 5.4% of fast molecules with speeds greater than 1000 m/s (Figure 3.2).

Each column is constructed with its base covering the velocity range it refers to and the area of each column is proportional to the percentage of molecules whose velocity lies within this range.

It is also possible to calculate the distribution of molecules over the energy of their translatory motion.

The number of molecules whose energy is more than double the average is less than 10%. The fraction of still more "energetic" molecules falls off faster and faster as the energy increases. Thus, the number of molecules whose energy is at least four times as large as the average is only 0.7%, eight times as large as the average $0.06 \times 10^{-4}\%$, 16 times as large as the average $2 \times 10^{-8}\%$.

The energy of an oxygen molecule moving with a speed of 11 km/s is equal to 32×10^{-12} erg. The average energy of a molecule at room temperature is equal to only 6×10^{-14} erg. Therefore, the energy of an "eleven-kilometre molecule" is at least 500 times as great as the energy of a molecule with the average speed. It is not surprising that the fraction of the molecules with speeds higher than 11 km/s is equal to an unimaginably small number—of the order of 10^{-300}.

But why are we intrigued with the speed of 11 km/s? In the first book we spoke of the fact that only bodies having this speed can escape from the Earth. Hence, molecules which have risen to a great height can lose their ties to the Earth and take off in a distant interplanetary trip, but for this it is necessary to have a speed of 11 km/s. The fraction of such fast molecules, as we have seen, is so negligible that there is no danger of the Earth's losing its atmosphere even in the course of a thousand million years.

The rate of leaving the atmosphere depends to an extraordinarily great degree on the gravitational energy GMm/r. If the average kinetic energy of a molecule is many times less than the gravitational energy, the escape of the molecules from the Earth is practically impossible. The gravitational energy on the surface of the Moon is 20 times as small, which gives an oxygen molecule a "runaway" energy of 1.5×10^{-12} erg. This value exceeds that of the average kinetic energy of a molecule by a factor of only 20-25. The fraction of the molecules capable of breaking away from the Moon is equal to 10^{-17}. This is already entirely different than 10^{-300}, and computations show that the air would leave the Moon quickly enough for interplanetary space. It is not surprising that there is no atmosphere on the Moon.

Thermal Expansion

If a body is heated, the motion of its atoms (molecules) will be more intensive. They will start pushing each other away and will occupy more space. The following well-known fact is explained by this: solids, liquids and gases expand when heated.

We don't have to say much about the thermal expansion of gases: in fact, the proportionality of gas temperature to volume was made the basis of our temperature scale.

We see from the formula $V = V_0T/273$ that the volume of a gas under a constant pressure grows by 1/273 (i.e. by 0.0037) of its value at 0 °C for each 1 °C increase in temperature (this situation is sometimes called Gay-Lussac's law).

Under ordinary conditions, i.e. at room temperature and standard atmospheric pressure, most liquids expand one-third to one-half as much as gases.

We have already spoken more than once of the anomalous expansion of water. The volume of water decreases as it is heated up from 0 to 4 °C. This anomaly in the expansion of water plays a colossal role in organic life on the Earth. In autumn, the upper layers of water become denser and sink to the bottom as they cool off. Warmer water, rising from below, takes their place. But such a mixing takes place only until the temperature of the water falls to 4 °C. With a further fall in temperature, the upper layers will no longer contract, will therefore not become heavier and will not sink to the bottom. Starting with this temperature, the upper layer, gradually cooling off, reaches zero degrees and freezes.

It is only this peculiarity of water that prevents rivers from freezing down to their beds. If water were to suddenly lose its remarkable anomaly, the disastrous consequences of this can be easily pictured even by a person without a rich imagination.

The thermal expansion of solids is considerably less than that of liquids. It is hundreds and thousands of times less than the expansion of gases.

Thermal expansion is an annoying hindrance in many cases. Thus, a change in the sizes of the moving parts of a clockwork with a change in temperature would lead to a change in the speed of the clock, if a special alloy, invar (invariant means unchanging, whence the name "invar"), were not used for these delicate components. Invar, steel with a large nickel content, is widely used in the instrument manufacture. An invar rod is lengthened by only one-millionth when its temperature increases by 1 °C.

An apparently negligible thermal expansion of a solid body can lead to serious consequences. The reason for this is that the low compressibility of solids makes it hard to hinder their thermal expansion.

When heated by 1 °C, a steel rod will increase in length by only one-hundred-thousandth, i.e. by an amount unnoticeable to the unaided eye. However, in order to prevent the expansion and compress the rod one-hundred-thousandth, a force of 20 kgf on 1 cm^2 is needed. And this is merely for cancelling the effect of a rise in temperature by only 1 °C.

The forces arising from thermal expansion can lead to breakages and catastrophes if they are not reckoned with. Thus, in order to avoid the action of these forces, the rails of a railroad-bed are laid with clearances. One has to remember these forces when handling glassware which is easily cracked by non-uniform heating. It is therefore the practice in laboratories to use vessels made of quartz glass (fused quartz, silicon dioxide, exists in an amorphous state), which lack this drawback. For one and the same rise in temperature, a copper bar will be lengthened by a millimetre, while the same sized bar of quartz glass will change its length by the unnoticeable amount of 30-

40 μm. The expansion of quartz is so insignificant that a quartz vessel can be heated by several hundred degrees and then thrown into water without any fear.

Heat Capacity

The internal energy of a body depends, of course, on its temperature. The more a body must be heated, the greater is the energy required. In order to raise the temperature of a body from T_1 to T_2, it is required to supply an energy

$$Q = C\,(T_2 - T_1)$$

to it in the form of heat. Here C is the proportionality factor, which is called the *heat capacity* of the body. The definition of the concept of heat capacity follows from the formula: C is the amount of heat necessary for raising the temperature by 1 °C. The heat capacity also depends on the temperature: rises in temperature from 0 to 1 °C and from 100 to 101 °C require somewhat different amounts of heat.

The quantity C is usually referred to a unit mass and called the *specific heat*. It is then denoted by the small letter c.

The amount of heat which goes to heat up a body of mass m is given by the following formula:

$$Q = mc\,(T_2 - T_1)$$

In what follows we shall make use of the concept of specific heat capacity, but shall speak of the heat capacity of a body for the sake of conciseness. An additional guide will always be the dimension of the quantity.

The value of heat capacity varies within a rather wide range. Of course, the heat capacity of water in calorie per degree is equal to unity by definition.

Most bodies have a heat capacity less than that of water. Thus, most oils, alcohols and other liquids have heat capacities close to 0.5 cal/g·K. Quartz, glass and sand have a heat capacity of the order of 0.2 cal/g·K. The heat capacity of iron and copper is about 0.1 cal/g·K. And here are examples of the heat capacities of some gases: hydrogen, 3.4 cal/g·K; air, 0.24 cal/g·K.

The heat capacities of all bodies decrease, as a rule, with a fall in temperature, and assume negligible values for most bodies at temperatures close to absolute zero. Thus, the heat capacity of copper is equal to only 0.0035 at 20 K; this is twenty-four times less than at room temperature.

A knowledge of heat capacities may prove useful for solving various problems on the distribution of heat among bodies.

The difference between the heat capacities of water and soil is one of the causes determining the distinction between maritime and continental climates. Possessing approximately five times as great a heat capacity as soil, water warms up slowly and cools off just as slowly.

In summer in maritime regions, the water, having warmed up more slowly than the land, cools the air, but in winter, the warm sea gradually cools off, yielding heat to the air and making the frost less severe. It is not difficult to calculate that 1 m^3 of sea water, cooling off by 1 °C, warms up 3000 m^3 of air by 1 °C. Consequently, in maritime regions the variations in temperature and the difference between winter and summer temperatures are less substantial than in continental regions.

Thermal Conductivity

Each object can serve as a "bridge" along which heat passes from a warmer body to a cooler one. For example, a tea spoon placed in a glass of hot tea is such a bridge.

Metallic objects conduct heat very well. The top of the spoon placed in the glass will become warm in the course of a second.

If it is necessary to stir a hot mixture, the handle of the stirrer must be made of wood or plastic. These solids conduct heat a thousand times worse than metals. We say "conduct heat", but could just as well have said "conduct cold". Of course, the properties of a body do not change as a result of the direction in which a heat flow is passing through it. In freezing weather we are careful not to touch metals with our bare hands outdoors, but grasp wooden handles without fear.

Among the poor heat conductors, they are also called heat insulators, are wood, brick, glass and plastic. The walls of houses, ovens and refrigerators are made of these materials.

Among the good conductors are all the metals. The best conductors are copper and silver—they conduct heat twice as well as iron.

Of course, not only solids can serve as "bridges" for the transfer of heat. Liquids also conduct heat, but much worse than metals. The thermal conductivity of'metals is hundreds of times greater than that of solid and liquid non-metallic bodies.

In order to demonstrate the poor thermal conductivity of water, the following experiment is performed. A piece of ice is fastened to the bottom of a test tube filled with water, while the top of the test tube is heated over a gas burner; the water begins boiling, but the ice is still not melting. If the test tube were without water and made of metal, then the piece of ice would begin melting almost immediately. Water conducts heat about two hundred times worse than copper.

Gases conduct heat tens of times worse than condensed non-metallic bodies. The thermal conductivity of air is twenty thousand times smaller than that of copper.

The poor thermal conductivity of gases permits us to hold in our hands a piece of dry ice whose temperature is —78 °C, and to even hold on our palms a drop of liquid nitrogen having a temperature of —196 °C. If we do not squeeze these cold objects with our fingers, there will be no "burn". The reason consists in the fact that when the drop of liquid or the piece of solid is boiling very energetically, it is covered by a "vapour jacket", and the layer of gas so formed serves as a heat insulator.

The spheroidal state of a liquid, this is what one calls the state in which drops are covered by vapour, is formed whenever water gets into a very hot frying-pan. Drops of boiling water, having fallen on one's palm, severely burn one's hand, although the difference in temperature between boiling water and a human body is less than that between a hand and liquid air. Since one's hand is colder than the drops of boiling water, heat leaves the drops, the boiling ceases and no vapour jacket is formed.

It isn't hard to understand that the best heat insulator is a vacuum—emptiness. There are no carriers of heat in a vacuum, and so the thermal conductivity will be at a minimum.

Therefore, if we want to create a thermal shield, hide something warm from something cold or vice versa, the best thing to do is to erect a casing with double walls and pump the air out of the space between them. When doing this, we come across the following curious phenomenon. If we keep track of the change in thermal conductivity of the gas as it is being rarefied, we shall observe that right until the moment when the pressure reaches several millimetres of mercury column the thermal conductivity remains practically constant. Our expectations are only justified when, with the passage to a higher vacuum, the thermal conductivity sharply falls off.

But what is the cause of this?

In order to understand this phenomenon, we must try to visualize the process of heat transfer in a gas.

Heat transfer from a warm place to a cold one takes place by means of the transmission of energy from one molecule to a neighbouring one. It is clear that collisions between fast and slow molecules usually lead to an acceleration of the slow molecules and a deceleration of the fast ones. And this means that the hot place will become colder, while the cold place will warm up.

But how will a decrease in pressure affect heat transfer? Since a decrease in pressure lowers the density, the number of collisions between fast and slow molecules, during which a transmission of energy occurs, will also decrease. This would decrease the thermal conductivity. However, a decrease in pressure leads, on the other hand, to an increase in the mean free path of the molecules, which therefore transfer heat by greater distances, and this tends to increase the thermal conductivity. Computations show that these effects compensate for each other, and so the ability to transfer heat does not change for some time as the air is being pumped out.

This will be the case until the vacuum becomes so considerable that the mean free path is comparable to the distance between the walls of the vessel. Now a further decrease in the pressure can no longer change the mean free path of the molecules, which are "hopping around" from wall to wall: the fall in density is not compensated for, and so the thermal conductivity rapidly falls in proportion to the pressure, reaching negligible values as a high vacuum is attained. The construction of a vacuum bottle is based on the use of the properties of a vacuum. Vacuum bottles are very widespread: they are applied not only for the conservation of hot and cold foods but also in science and technology. In such a case they are called Dewar flasks (vessels), in honour of their inventor. Liquid air, nitrogen and oxygen are transported in such vessels. Later we shall tell how these gases are obtained in a liquid state*.

Convection

But if water is such a poor heat conductor, how does it warm up in a tea-kettle? Air conducts heat even worse; then it isn't clear why the same temperature is established in all parts of a room.

Water in a tea-kettle quickly boils because of gravity. The lower layers of water, having warmed up, expand, become lighter and rise to the top, with cold water taking their place. A rapid heating occurs thanks only to *convection* (derived from the Latin *convectus* meaning "bring together"). It wouldn't be so easy to heat up water in a tea-kettle located in an interplanetary rocket.

Somewhat earlier explaining why rivers do not freeze down to the bottom, we spoke of another case of convection currents of water without using this word.

Why are the radiators of a central heating placed near the floor? Why is the ventilation window made in the upper part of a window? It might be more convenient to open a ventilation window if it were lower down, and it might not be a bad idea to place radiators under the ceiling, so that they did not get in the way. If we were to follow such advice, we would soon discover that the room is not being warmed up by the radiator and not being aired when the ventilation window is open.

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*Everyone who has seen cylinders of vacuum bottles noticed that their walls are always silver-plated. But why? The fact is that thermal conductivity is not the only means of transferring heat. There exists yet another way to transfer heat, which we shall speak of in another book, so-called radiation. Under ordinary conditions, it is much weaker than thermal conductivity, but is nevertheless quite noticeable. The walls of vacuum bottles are covered with a coating of silver precisely in order to weaken the radiation.

The same thing takes place with the air in a room as with the water in a tea-kettle. When the radiator is turned on, the air in the lower layers of the room begins warming up. It expands, becomes lighter and rises towards the ceiling. Heavier layers of cold air arrive in its place. And they, having warmed up, leave for the ceiling. A continuous air current thus arises in the room, with warm air moving up from below and cold air moving down from above. Opening a ventilation window in winter, we admit a stream of cold air into the room. It is heavier than the air in the room, and so goes down, forcing out the warm air, which rises towards the top of the room and leaves through the ventilation window.

A kerosene lamp flames up well only when it is covered with a tall piece of glass. One should not think that the glass is needed only in order to shield the flame from the wind. Even in the calmest weather, the brightness of the flame immediately increases when the glass is put on the lamp. The role of the glass consists in intensifying the stream of air approaching the flame—in creating a draught. This occurs because the air inside the glass, deprived of the oxygen that was used for the burning, quickly warms up and rises, while pure cold air moves into its place through the holes made in the burner of the lamp.

The taller the glass, the better will the lamp burn. In fact, the speed with which cold air rushes into the burner of the lamp depends on the difference in weight between the heated column of air in the lamp and the cold air outside it. The higher the column of air, the greater this difference in weight, and so the faster the movement.

Factory chimneys are also made high for this reason. An especially rapid influx of air, a good draught, is needed for a factory furnace. It is achieved as a result of a high chimney.

The lack of convection in a rocket devoid of weight makes it impossible to use matches, lamps or gas burners:

the products of combustion would smother the flame.

Air is a poor conductor; we can conserve heat with its aid, but only under one condition: if we avoid convection, the mixing of warm and cold air, which will bring to naught the thermal-insulation properties of air.

The elimination of convection is achieved by applying various kinds of porous and fibrous bodies. It is difficult for air to move inside such bodies. All bodies of this kind are good heat insulators, thanks only to their ability to retain a layer of air. But the thermal conductivity of the substance itself of which the fibres or the walls of the pores consist can be not very small.

A good fur coat is made of a dense fur containing as many fibres as possible; eiderdown can be used to make warm sleeping bags weighing less than half a kilogram, due to the exceptional thinness of its fibres. Half a kilogram of this down can "detain" as much air as tens of kilograms of sheet wadding.

Storm windows are made in order to reduce the convection. The air between the panes does not participate in the mixing of layers of air which takes place within the room.

On the contrary, every movement of the air intensifies the mixing and increases the transfer of heat. This is precisely why we fan ourselves or turn on the ventilator when we want the heat to go away faster. This is also what makes it colder in the wind. But if the air temperature is higher than one's body temperature, the mixing has the opposite effect, and a wind feels like a hot breath of air.

The problem involved in a steam boiler consists in obtaining steam heated to the required temperature as quickly as possible. The natural convection in a gravitational field is quite insufficient for this. Therefore, the creation of an intensive circulation of water and steam, leading to the mixing of warm and cold layers, is one of the basic problems in the construction of steam boilers.

4. States of Matter

Iron Vapour and Solid Air

A strange combination of words, isn't it? However, this is by no means nonsense: iron vapour and solid air exist in nature, only not under ordinary conditions.

But what conditions are we talking about? The state of a substance is determined by two circumstances: temperature and pressure.

Our lives proceed under conditions which change relatively little. The air pressure varies by several per cent about a value of one atmosphere; the temperature of the air, say, near Moscow, lies in the interval from −30 to +30 °C; in the absolute scale, in which the lowest possible temperature (−273 °C) is taken as zero, this interval will look less impressive: 240-300 K, which is also only ±10% of the average value.

It is quite natural that we have become accustomed to these ordinary conditions, and so when speaking simple truths such as "iron is a solid, air is a gas", we forget to add "under standard conditions".

If iron is heated, it will first melt and then vaporize. If air is cooled, it will first liquefy and then solidify.

Even if the reader has never come across iron vapour or solid air, he or she will probably believe without difficulty that by means of a change in temperature it is possible to obtain any substance in a solid, liquid and gaseous state or, as is also said, in a solid, liquid or gaseous phase.

It is easy to believe this because everyone has observed a substance without which life on the Earth would be impossible, and that substance is in the form of a gas, a liquid, or a solid. We are speaking, of course, of water.

But under what conditions does a transformation of a substance from one state to another occur?

Boiling

If we lower a thermometer into water which has been poured into a tea-kettle, turn on the electric stove and watch the mercury in the thermometer, we shall see the following: the level of the mercury will inch upwards almost immediately. Now it is already 90, 95 and finally 100 °C. The water begins boiling and simultaneously the mercury stops rising. The water has already been boiling for many minutes, but the level of the mercury does not change. The temperature will not change until all the water has boiled away (Figure 4.1).

But what is the heat used for if the temperature of the water does not change? The answer is obvious. The process of transforming water into steam requires energy.

Let us compare the energy of a gram of water and a gram of the steam created out of it. The molecules of the steam are distributed farther from each other than the water molecules. It is obvious that because of this the potential energy of the water will differ from that of the steam.

The potential energy of attracting particles decreases as they approach. The energy of the steam is therefore greater than that of the water, and so the transformation of water into steam requires energy. This excess energy is imparted by the electric stove to the water boiling in the tea-kettle.

The energy needed for transforming water into steam is called its *heat of vaporization*. In order to transform 1 g of water into steam, 539 calories are required (this figure

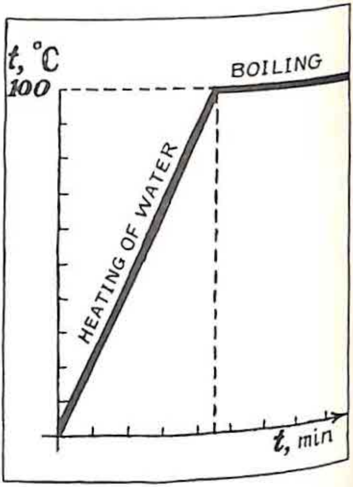


Figure 4.1

is for a temperature of 100 °C). If 539 calories are used for 1 g, then 18 × 539 ≈ 9700 calories will be supplied to 1 mole of water. This amount of heat must be consumed in breaking the intermolecular bonds. One can compare this figure with the amount of work necessary for breaking the intramolecular bonds. In order to split one mole of steam into atoms, about 220 000 calories are required, i.e. 25 times as much energy. This directly proves the weakness of the forces binding molecules to each other, as compared to the forces finding atoms together in a molecule.

Dependence of Boiling Point on Pressure

The boiling point of water is equal to 100 °C; one might think that this is an inherent property of water, that water will always boil at 100 °C, no matter where and under what conditions it may be.

But this is not so, and people who live high up in the mountains are perfectly well aware of this.

There is a tourist cabin and a scientific station near the top of Mt. Elbrus. Novices are sometimes amazed at "how hard it is to boil an egg in boiling water" or wonder "why boiling water doesn't scald". In such cases, it is pointed out to them that water is already boiling at 82 °C on the top of Mt. Elbrus.

But what causes this? What physical factor interferes with boiling? And does the height above sea level have any significance?

This physical factor is the pressure acting on the surface of the liquid. It isn't necessary to climb to the top of a mountain in order to check the validity of what we have said.

If we place a bell glass over water that is being heated and pump air into or out of it, we can convince ourselves that the boiling point is raised by an increase in pressure and lowered by a decrease in pressure.

Water boils at 100 °C only at a definite pressure—760 mm Hg (or 1 atm).

The curve showing the dependence of the boiling point on the pressure is depicted in Figure 4.2. The pressure is equal to 0.5 atm on the top of Mt. Elbrus, and a boiling point of 82 °C corresponds to this pressure.

But it is even possible to refresh oneself in hot weather with water boiling at 10-15 mm Hg. At such pressures, the boiling point will fall to 10-15 °C.

One can even obtain "boiling water" having a temperature of freezing water. One has to lower the pressure to 4.6 mm Hg for this.

It is possible to observe an interesting scene by placing an uncovered vessel with water under a bell glass and pumping the air out. This will make the water boil, but boiling requires heat. But since there is no air, the water has to give up its own energy. The temperature of the

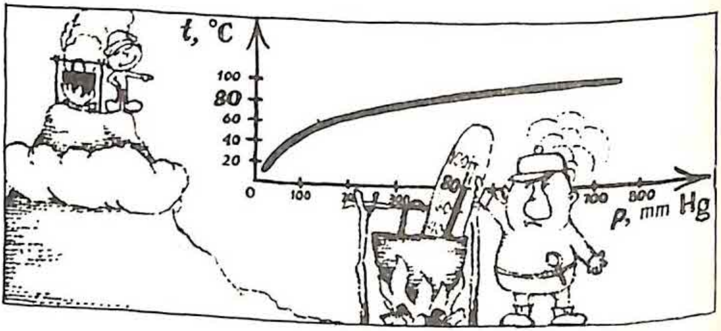


Figure 4.2

boiling water starts falling, but since the pumping continues, the pressure also falls. Therefore, the boiling will not cease, the water will continue cooling off and will finally freeze.

Such a boiling of cold water occurs not only as a result of air being pumped out. For example, when a marine screw propeller rotates, the pressure in the layer of water moving rapidly about the metallic surface will fall sharply, and so the water in this layer will boil, i.e. many bubbles filled with steam will appear in it. This phenomenon is called *cavitation* (from the Latin *cavus* meaning "hollow").

Decreasing the pressure, we lower the boiling point. And raising it? A graph analogous to ours answers this question. A pressure of 15 atm can so delay boiling of water that it will begin only at 200 °C, while a pressure of 80 atm will make water boil only at 300 °C.

Thus, a definite boiling point corresponds to a definite external pressure. But we may also turn this assertion "around" by saying that "a definite pressure corresponds to each boiling point of water". This pressure is called the *vapour pressure.*

The curve depicting the dependence of the boiling point on the pressure is simultaneously the curve of the vapour pressure as a function of the temperature.

The numbers plotted on the boiling point graph (or on the vapour pressure graph) show that the vapour pressure changes very sharply with a change in the temperature. At 0 °C (i.e. 273 K) the vapour pressure is equal to 4.6 mm Hg, at 100 °C (373 K) it equals 760 mm Hg, i.e. has increased by a factor of 165. With a doubling of the temperature from 0 °C (i.e. 273 K) to 273 °C (i.e. 546 K), the vapour pressure grows from 4.6 mm Hg to almost 60 atm, i.e. by a factor of about 10 000.

Therefore, the boiling point, on the contrary, changes rather slowly with a change in the pressure. When the pressure is doubled, from 0.5 to 1 atm, the boiling point grows from 82 °C (i.e. 355 K) to 100 °C (i.e. 373 K), and with a doubling from 1 to 2 atm, from 100 °C (i.e. 373 K) to 120 °C (i.e. 393 K).

The same curve that we are now considering also controls the condensation of steam into water.

Steam can be transformed into water by either compressing or cooling it.

During the course of condensation, just as for boiling, the point will not move off the curve until the transformation of steam into water or water into steam is completely finished. This can also be formulated as follows: the coexistence of the liquid and the vapour phase is possible under the conditions of our curve and only under these conditions. If, moreover, no heat is supplied or removed, the amount of vapour and liquid in a closed vessel will remain constant. We say that such a vapour and liquid are in equilibrium, and a vapour in equilibrium with its liquid is called saturated.

The boiling and condensation curve has, as we see, yet another meaning—it is the curve of the equilibrium of liquid and vapour. The equilibrium curve divides the plane of the diagram into two parts. To the left and above the curve (towards higher temperatures and lower pressures) is the stable-vapour region. To the right and below the curve is the stable-liquid region.

The vapour-liquid equilibrium curve, i.e. the curve of the dependence of the boiling point on the pressure, or, what is the same thing, of the vapour pressure on the temperature, is approximately identical for all liquids. In some cases, the change may be somewhat sharper, in others somewhat slower, but the vapour pressure always grows rapidly with rise in temperature.

We have already used the words "gas" and "vapour" many times. These two words are more or less synonyms. One may say: water gas is the vapour of water, oxygen gas is the vapour of liquid oxygen. Nevertheless, a certain habit has been formed regarding the usage of these two words. Since we are accustomed to a definite, rather small range of temperatures, we usually apply the word "gas" to those substances whose vapour pressure is higher than atmospheric pressure at standard temperatures. On the contrary, we speak of a vapour when a substance is more stable in the form of a liquid at room temperature and atmospheric pressure.

Evaporation

Boiling is a rapid process, and not even a trace of boiling water remains after a short time—it is transformed into steam.

But there is also another phenomenon whereby water or some other liquid is transformed into a vapour—*evaporation*. Evaporation takes place at any temperature and regardless of the pressure, which is always close to 760 mm Hg under ordinary conditions. Evaporation, unlike boiling, is a very slow process. A bottle of eau-de-cologne which we forgot to close will turn out to be empty after several days; water will remain in a saucer for a longer time, but sooner or later it too will turn out to be dry.

Air plays a big role in the process of evaporation. It does not, by itself, prevent water from evaporating. As soon as we uncover the surface of a liquid, water molecules will begin moving into the nearest layer of air. The density of the vapour in this layer will quickly increase; after a short time, the pressure of the vapour will become equal to the vapour pressure at the temperature of the surroundings. Moreover, the vapour pressure will be exactly the same as in the absence of air.

The passage of vapour into the air does not, of course, mean an increase in pressure. The total pressure in the space on top of the water surface does not increase; it is only the fraction of this pressure which is borne by the vapour that increases, and the fraction of the air correspondingly decreases as it is displaced by the vapour.

There is vapour mixed with air over the water; higher up are layers of air without vapour. They will inevitably mix. Water vapour will continually move into higher layers, and its place in the lower layer will be taken by air which does not contain any water molecules. Therefore, room will always be made for new water molecules in the layer closest to the water. Water will continually evaporate, maintaining the pressure of the water vapour at the surface equal to the vapour pressure, and the process will continue until the water has completely evaporated.

We began with examples involving eau-de-cologne and water. It is well known that they evaporate with different speeds. Ether flies away with exceptional rapidity, alcohol is rather quick and water is much slower. We shall immediately understand why this is so if we find the values of the vapour pressure for these liquids in a handbook, say, at room temperature. Here are the figures:

ether—437 mm, alcohol—44.5 mm and water—17.5 mm Hg.

The greater the vapour pressure, the more vapour there will be in the adjacent layer of air and the faster the liquid will evaporate. We know that vapour pressure increases with temperature. It is clear why the rate of evaporation increases with heating.

It is also possible to influence the rate of evaporation by other means. If we want to aid the evaporation, we must take the vapour away from the liquid more rapidly, i.e. speed up the mixing with air. This is precisely why evaporation is greatly speeded up by blowing on the liquid. Water, although it has a relatively low vapour pressure, will disappear rather quickly if the saucer is placed in the wind.

It is therefore clear why a swimmer, having come out of the water, feels cold in the wind. The wind speeds up the mixing of air with vapour and so increases the rate of evaporation, but the swimmer's body is forced to give up heat for the evaporation.

The way a person feels depends on how much water vapour there is in the air. Both dry and moist air are unpleasant. The humidity is regarded as standard when it is equal to 60%. This means that the density of water vapour is 60% of the density of saturated water vapour at the same temperature.

If moist air is cooled, the pressure of the water vapour in it will eventually equal the vapour pressure at this temperature. The vapour will become saturated and will begin condensing into water with a further fall in temperature. The morning dew moistening the grass and the leaves appears precisely as a result of this phenomenon.

At 20 °C the density of saturated water vapour is about 0.000 02 g/cm^3. We shall feel fine if the amount of water vapour in the air is 60% of this figure, only a bit more than one-hundred-thousandth of a gram per cubic centimetre.

Although this is a small number, it leads to an impressive amount of water in a room. It is not difficult to calculate that in an average sized room of 12-m^2 area and 3-m height, "there will be room" for about a kilogram of water in the form of saturated vapour.

Consequently, if we place an open barrel of water in a room sealed up tight, then, regardless of the barrel's volume, a litre of water will evaporate.

It is interesting to compare this result for water with the corresponding figures for mercury. At the same temperature of 20 °C, the density of saturated mercury vapour is 10^{-8} g/cm^3. There will be room for at least 1 g of mercury vapour in a room of the size we have just considered.

Incidentally, mercury vapour is very poisonous, and one gram of it can seriously injure any person's health. When working with mercury, it is necessary to see to it that not even the smallest drop is spilt.

Critical Temperature

How can we turn a gas into a liquid? The boiling point graph answers this question. A gas can be turned into a liquid by either lowering the temperature or raising the pressure.

In the 19th century, the problem of raising pressures seemed to be easier than that of lowering temperatures. At the beginning of that century, the great English physicist Michael Faraday (1791-1867) succeeded in compressing gases to the value of their vapour pressures and in this manner transforming many gases (chlorine, carbon dioxide, etc.) into liquids.

However, certain gases, such as hydrogen, nitrogen, oxygen, simply could not be liquefied. No matter how much the pressure was increased, they did not turn into

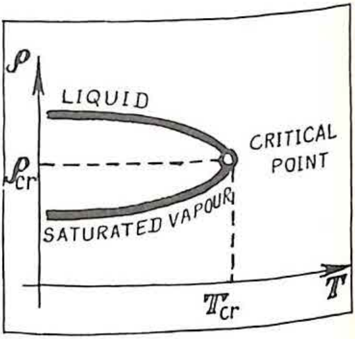


Figure 4.3

liquids. One might have thought that oxygen and other gases cannot be liquid. They were regarded as true, or constant, gases.

But as a matter of fact, the failures were caused by a lack of understanding of one important circumstance.

Let us consider a liquid and a vapour which are in equilibrium, and think of what happens to them with an increase in the boiling point and, of course, a corresponding increase in the pressure. In other words, let us imagine that a point on the boiling point graph is moving upwards along the curve. It is clear that as the temperature rises, the liquid expands and its density falls. But as for the vapour, an increase in the boiling point is, of course, conducive to its expansion, but, as we have already said, the pressure of the saturated vapour grows considerably faster than the boiling point. Therefore, the density of the vapour does not fall, but, on the contrary, rapidly rises with an increase in the boiling point.

Since the density of a liquid falls, and the density of a vapour rises, moving "upwards" along the boiling point curve, we shall inevitably arrive at the point for which the densities of the liquid and the vapour are equal (Figure 4.3).

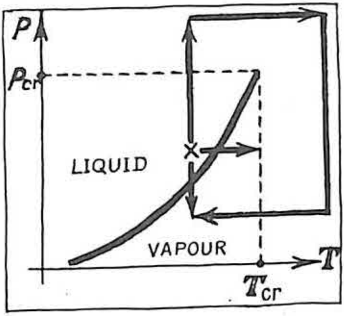
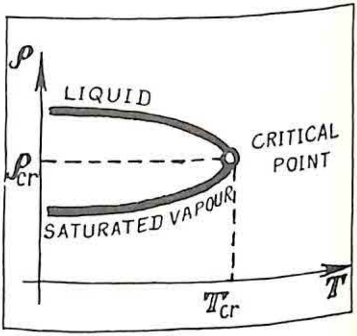


Figure 4.4

At this remarkable point, called *critical*, the boiling point curve breaks off. Since all distinctions between a gas and a liquid are related to a difference in density, the properties of the liquid and the gas become identical at the critical point. Each substance has its own critical temperature and critical pressure. Thus, the critical point for water corresponds to a temperature of 374 °C and a pressure of 218.5 atm.

If we compress a gas whose temperature is below critical, the process of its compression can be depicted by an arrow intersecting the boiling point curve (Figure 4.4). This implies that at the moment of attaining a pressure equal to the vapour pressure (the point of intersection of the arrow with the boiling point curve), the gas starts condensing into a liquid. If our vessel were transparent, then at this moment we would see a layer of liquid forming at the bottom of the vessel. If the pressure does not change, the layer of liquid will grow until all of the gas has finally been transformed into the liquid. A further compression will now require an increase in pressure.

The situation is entirely different for the compression of a gas whose temperature is above critical. The process of compression can again be still depicted in the form of an arrow going upwards. But now this arrow does not



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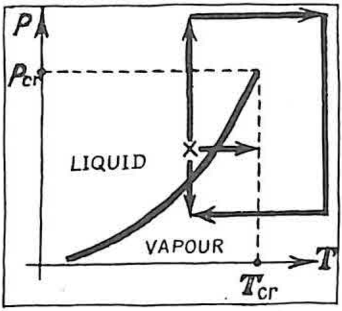

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The situation is entirely different for the compression of a gas whose temperature is above critical. The process of compression can again be still depicted in the form of an arrow going upwards. But now this arrow does not intersect the boiling point curve. Hence, during the compression the vapour will not condense, but will only continually become denser.

The existence of a gas-liquid interface is impossible at a temperature above critical. When compressed to arbitrary densities, a uniform substance will be found under the piston, and it is hard to say when one may call it a gas and when a liquid.

The presence of the critical point shows that there is no difference in principle between the liquid and gaseous states. At first sight, it might seem that there is no such difference in principle only in case we are dealing with temperatures above critical. This, however, is not so. The existence of the critical point indicates the possibility of transforming a liquid, a genuine liquid, which can be poured into a glass, into the gaseous state avoiding the boiling process.

The path of such a transformation is shown in Figure 4.4. An unquestionable liquid is marked by a cross. If we lower the pressure somewhat (arrow pointing downwards), it will boil; it will also boil in case we raise the temperature somewhat (arrow pointing to the right). But let us choose a different way. Let us compress the liquid so hard that its pressure exceeds critical. The point representing the state of the liquid will rise vertically. Then let us heat the liquid—this process will be depicted by a horizontal line. Now, after we have found ourselves to the right of the critical temperature, let us lower the pressure to its initial value. If we now decrease the temperature, we can obtain a most genuine vapour which could have been obtained from this liquid along a simpler and shorter path.

Therefore, by changing the pressure and temperature so that the critical point is avoided, it is always possible to obtain a vapour by means of a continuous transition from a liquid and vice versa. Such a continuous transition does not require boiling or condensation.

Early attempts to liquefy such gases as oxygen, nitrogen and hydrogen were unsuccessful because the existence of the critical temperature was unknown. These gases have very low critical temperatures: —119 °C for oxygen, —147 °C for nitrogen and —240 °C or 33 K for hydrogen. The record holder is helium, whose critical temperature is equal to 4.3 K. It is possible to transform these gases to the liquid phase in only one way: we must lower their temperatures below the indicated values.

Obtaining Low Temperatures

A significant decrease in temperature can be attained by various means. But the idea involved in all these methods is one and the same: we must force the body we want to cool to expend its internal energy.

But how can this be done? One of the ways is to make the liquid boil, not bringing in any heat from without. For this, as we know, it is necessary to decrease the pressure—to reduce it to the value of the vapour pressure. The heat expended on the boiling will be taken from the liquid, and hence the temperature of the liquid and vapour will fall; therefore, so will the vapour pressure. Consequently, in order that the boiling not cease but proceed more rapidly, it is necessary to continually pump air out of the vessel with the liquid.

However, a limit is reached to the fall in temperature during this process: the vapour pressure will eventually become completely negligible, and so even the most powerful pumps will be unable to create the required pressure.

In order to continue the lowering of temperature, we can, by cooling a gas with the aid of the liquid already obtained, convert it into a liquid with a lower boiling point. It is now possible to repeat the pumping process with the second substance and in this way to obtain lower temperatures. In case of necessity, such a cascade method of obtaining low temperatures can be extended.

Precisely in such a manner was this problem dealt with at the end of the past century, the liquefaction of gases was carried out in stages: ethylene, oxygen, nitrogen and hydrogen, substances with boiling points of —103, —183, —196 and —253 °C, were successively converted into liquids. Having liquid hydrogen available, one can also obtain the lowest boiling liquid—helium (—269 °C). The neighbour "to the left" helped obtain the neighbour "to the right".

The cascade method of cooling is about a hundred years old. Liquid air was obtained by this method in 1877. Liquid hydrogen was first obtained in 1884-1885. Finally, the last stronghold was taken after another twenty years: helium, the substance with the lowest critical temperature, was converted into a liquid in 1908 by Heike Kamerlingh Onnes (1853-1926) in Leiden, Holland. The 70th anniversary of this important scientific achievement was widely celebrated.

For many years, the Leiden laboratory was the only "low-temperature" laboratory. But now there exist tens of such laboratories in many countries, not to mention the factories producing liquid air, nitrogen, oxygen and helium for technical purposes.

The cascade method of obtaining low temperatures is now rarely applied. In technical installations for lowering temperatures, a different means of decreasing the internal energy of a gas is applied: the gas is forced to expand rapidly and perform work at the expense of its internal energy.

If, for example, air is compressed up to several atmospheres and let into an expander, then when it performs the work involved in displacing a piston or rotating a turbine, it will cool off so abruptly that it liquefies. If carbon dioxide is let out of a cylinder with great speed, it will cool off so abruptly that it is converted into "ice" in the air.

Liquid gases have found wide application in technology. Liquid oxygen is used for explosives and as a component of the fuel mixture in jet engines.

The liquefaction of air is used in technology for separating the gases constituting air.

The temperature of liquid air is widely used in various branches of technology. But this temperature isn't low enough for many physical investigations. In fact, if we convert the relevant temperatures expressed on the centigrade scale to their values on the Kelvin scale, we shall see that the temperature of liquid air is approximately one-third of room temperature. Much more interesting for physics are "hydrogen" temperatures, i.e. temperatures of the order of 14-20 K, and especially "helium" temperatures. The lowest temperature obtained by pumping out liquid helium is 0.7 K.

Physicists have succeeded in coming much closer to absolute zero. At the present time, temperatures have been obtained which are only several thousandths of a degree above absolute zero. However, these extremely low temperatures are obtained by methods which do not resemble those described above.

In recent years, cryogenics, the physics of low temperatures, has created the need leading to the founding of a new branch of industry. This branch is engaged in the manufacture of equipment and apparatus enabling large volumes and long conductors to be held at temperatures close to absolute zero.

Supercooled Vapours and Superheated Liquids

In passing through the boiling points, a vapour ought to condense, be transformed into a liquid. However, it turns out that if a vapour is very pure and does not come in contact with a liquid, we are able to obtain it in the form of a supercooled or supersaturated vapour—a vapour which should have already become a liquid a long time ago.

A supersaturated vapour is very unstable. Sometimes it is sufficient to shake the vessel containing the vapour or throw a couple of grains into it for the delayed condensation to immediately begin.

Experience shows that the condensation of steam molecules is greatly eased by the introduction of small alien particles. The supersaturation of water vapour does not occur in dusty air. It is possible to bring about condensation with puffs of smoke, since smoke consists of tiny solid particles. When the particles enter the steam, they gather molecules around themselves and become centres of condensation.

Thus, even though unstable, a vapour can exist in the region of temperatures fit for liquid "life".

But can a liquid "live" in the region of a vapour under those same conditions? In other words, is it possible to superheat a liquid?

It turns out to be possible. For this it is necessary to prevent the molecules of the liquid from breaking away from its surface. A radical means of achieving this is liquidating the free surface, i.e. placing the liquid in a vessel where it would be compressed on all sides by solid walls. Liquids have been successfully superheated in this manner by several degrees, i.e. one is able to displace a point depicting the state of a liquid to the right of its boiling point curve (see Figure 4.4).

Superheating is the displacement of a liquid into the region of a vapour; therefore, the superheating of a liquid can be achieved by lowering the pressure, as well as by supplying heat.

The former method can be used to obtain a surprising result. Water or some other liquid thoroughly freed of dissolved gases, which is not easy to do, is placed in a vessel with a piston reaching the surface of the liquid. The vessel and the piston should be wet by the liquid. If we now draw the piston towards ourselves, the water cohering to the bottom of the piston will move along with it. But the layer of water cohering to the piston will pull the next layer of water after it, this layer will pull the one lying below it. As a result, the liquid will stretch.

The column of water will finally break (it is precisely the column that will break, but the water will not break away from the piston), but this will occur when the force on a unit of area attains tens of kilograms. In other words, a negative pressure of tens of atmospheres is created in the liquid.

The vapour phase of a substance is stable even for small positive pressures. And a liquid can be made to have a negative pressure. You couldn't think of a more striking example of "superheating".

Melting

There is no solid body which would withstand a continual rise in temperature. Sooner or later a solid piece is transformed into a liquid; true, in certain cases we will not succeed in reaching the melting point—a chemical decomposition may take place.

Molecules move more intensively as the temperature increases. Finally, the moment arrives when the preservation of order among the wildly "swinging" molecules becomes impossible. The solid body melts. Tungsten

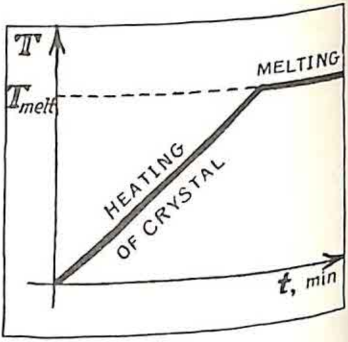

Figure 4.5

has the highest melting point: 3380 °C. Iron melts at 1539 °C, gold at 1063 °C. Incidentally, there are also easily melted metals. Mercury, as is well known, will even melt at a temperature of −39 °C. Organic substances do not have high melting points. Naphthalene melts at 80 °C, toluene at −94.5 °C.

It is not at all difficult to measure the melting point of a body, especially if it melts within the interval of temperatures which can be measured by an ordinary thermometer. It is completely unnecessary to keep one's eye on the melting body. It is sufficient to look at the mercury column of the thermometer. The temperature of the body increases until the melting begins (Figure 4.5). As soon as the melting begins, the rise in temperature ceases, and the temperature remains constant until the process of melting is completely finished.

Just as in the conversion of a liquid into a vapour, the conversion of a solid into a liquid requires heat. The amount of heat needed for this is called the *latent heat of fusion*. For example, the melting of one kilogram of ice requires 80 kcal.

Ice is one of the bodies possessing a large heat of fusion. The melting of ice requires, for example, more than ten times as much energy as the melting of the same mass of lead. Of course, we are talking about the melting proper; here we are not dealing with the fact that before lead begins to melt, it must be heated up to +327 °C. The thawing of snow is delayed as a result of the large heat of fusion of ice. Imagine that its heat of fusion were ten times smaller. Then the spring thaws would lead each year to inconceivable disasters.

Thus, the heat of fusion of ice is great, but it is also small if we compare it with the heat of vaporization—540 kcal/kg (about seven times as small). This difference, by the way, is completely natural. Converting a liquid into a vapour, we must tear its molecules away from each other, but in melting a solid, we only have to destroy the order in the distribution of the molecules, leaving them almost at the same distances from each other. It is clear that less work is required in the latter case.

The possession of a definite melting point is an important feature of crystalline substances. It is on the basis of precisely this property that they are easily distinguished from other solids, called amorphous bodies or glasses. Glasses are found among organic substances as well as among inorganic ones. Window glass is usually made out of silicates of sodium and calcium; an organic glass (it is also called Plexiglas) is often placed on a desk.

In contrast to crystals, amorphous substances do not have a definite melting point. Glass does not melt, but softens. When heated, a piece of hard glass becomes soft, so that it can be easily bent or stretched; it begins to change its form at a higher temperature under the influence of its own weight. As it is further heated, the thick viscous mass of glass assumes the form of the vessel in which it is lying. This mass is at first as thick as honey, then as sour cream and, finally, becomes almost like a liquid with a small viscosity, such as water. With the best will in the world, here we are unable to single out a definite temperature at which the solid entered the liquid phase. The reasons for this lie in the radical difference between the structure of glass and that of crystalline bodies. As has been said above, the atoms in amorphous bodies are distributed disorderly. The structure of glass resembles that of a liquid. The molecules in hard glass are already distributed disorderly. Hence, a rise in the temperature of glass merely increases the amplitude of the oscillations of its molecules, gradually giving them more and more freedom of movement. Therefore, glass softens gradually and does not display the sharp transition from "solid" to "liquid", which is characteristic of a transition from the distribution of molecules in a strict order to their disordered distribution.

When discussing a boiling point curve, we said that a liquid and a vapour can exist, although in an unstable state, in alien regions—a vapour can be supercooled and moved to the left of the boiling point curve, while a liquid can be superheated and drawn off to the right of the boiling point curve.

Are the analogous phenomena with respect to a crystal and a liquid possible? It turns out that the analogy here is incomplete.

If a crystal is heated, it will begin melting at its melting point. We shall not succeed in superheating a crystal. On the contrary, in cooling a liquid, we can, if we take certain steps, "slip past" the melting point with comparative ease. We are able to achieve considerable supercoolings of certain liquids. There are even such liquids which are easy to supercool, but hard to make them crystallize. As such a liquid is cooled, it becomes more and more viscous and finally hardens without having crystallized. Glass is like that.

It is also possible to supercool water. Drops of mist can fail to freeze even during the most severe frosts. If a crystal of a substance (priming) is thrown into a supercooled liquid, then crystallization will immediately begin.

Finally, in many cases a delayed crystallization can begin as a result of shaking or other random events. It is known, for example, that crystalline glycerine was first obtained while being transported by train. After lying around for a long time, glass can begin to crystallize (devitrify).

How to Grow a Crystal

Under definite known conditions, crystals can be grown from almost any substance. Crystals can be obtained from a solution or from a melt of the given substance, as well as from its vapour (black rhombic crystals of iodine, for instance, are readily deposited from iodine vapour at standard pressure without an intermediate conversion into the liquid state).

Start by dissolving common salt or sugar in water. At room temperature (20 °C), you can dissolve up to 70 g of salt in a thick glass (holding about 200 g of water). If you keep adding salt, it will not dissolve, but will settle to the bottom in the form of a residue. A solution that can dissolve no more solute (as it is called) is said to be saturated with the given substance. If we change the temperature, the solubility of the solute in the solvent is changed as well. Everyone knows that hot water dissolves most substances more readily than cold water.

Imagine now that you have prepared a saturated solution, say, of sugar, at a temperature of 30 °C and cool it to 20 °C. At 30 °C, you can dissolve 223 g of sugar in 100 g of water, and at 20 °C, only 205 g. Then, in cooling from 30 to 20 °C, 18 g of sugar turn out to be "redundant" and, as they say, are precipitated from the solution. Hence, one of the possible ways to obtain crystals is to cool a saturated solution.

We can accomplish the same in a different way. Prepare a saturated solution of salt and let it stand in an open glass. After some time has passed you will find crystals of salt at the bottom. Why did they form? Look at the glass again, more carefully, and you can see that another change occurred together with the appearance of crystals: there is less water. The water evaporated and left "redundant" matter in the solution. Thus, still another way to form crystals is to evaporate the solution.

How are crystals formed from a solution?

We mentioned that the crystals precipitate from the solution. Does this mean that no crystal was observed for a whole week and then, in a flash, it appears as if by magic? No, this is not so; crystals grow. You cannot, of course, observe the initial instant of growth with the naked eye. First, a few of the randomly moving molecules or atoms of the solute assemble by chance in approximately the same order required to form the crystal lattice. Such a group of atoms or molecules is called a *nucleus*.

Experiments show that nuclei are more frequently formed when the solution contains extremely fine particles, dust specks, of some foreign substance. Crystallization proceeds at the highest rate and most easily if a tiny seed crystal is put into the saturated solution. Then the precipitation of the solid substance from the solution consists in the growth of the seed crystal rather than in the formation of new small crystals, i.e. in nucleation.

The growth of a nucleus does not, of course, differ in any way from the growth of a seed crystal. The advantage of using a seed crystal is that it "draws" to itself the substance separating out of the solution, hindering, in this way, the formation of a large number of nuclei. If a great many nuclei are formed at once, they impede each other in growing and we cannot obtain large crystals.

How do new portions of atoms or molecules, separating out of the solution, arrange themselves on the surfaces of the nucleus?

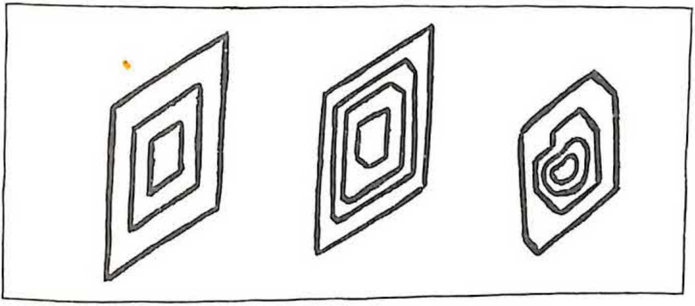

Figure 4.6

It has been found that the growth of a nucleus or seed crystal consists in the seemingly outward motion of its faces in a direction perpendicular to each face so that they remain parallel to their initial positions (the crystal seems to expand). Naturally, the angles between the faces remain constant (we already know that the constancy of these angles is one of the vital features of crystals and is due to their lattice structure).

The successive outlines during the growth of three different crystals of the same substance are shown in Figure 4.6. Similar pictures can be observed in a microscope. For the crystal shown at the left the number of faces remains constant during the growth. The middle crystal is an example of how a new face appears during the growth (at the upper right) and subsequently disappears.

It is important to note that the rate of growth of the faces, i.e. the velocity at which the faces seem to move while remaining parallel to their initial positions, is not the same for various faces. We also find that the faces that disappear are those that grow fastest, for instance, the lower left face in the middle crystal. The slowest-growing faces, on the contrary, become the widest or,

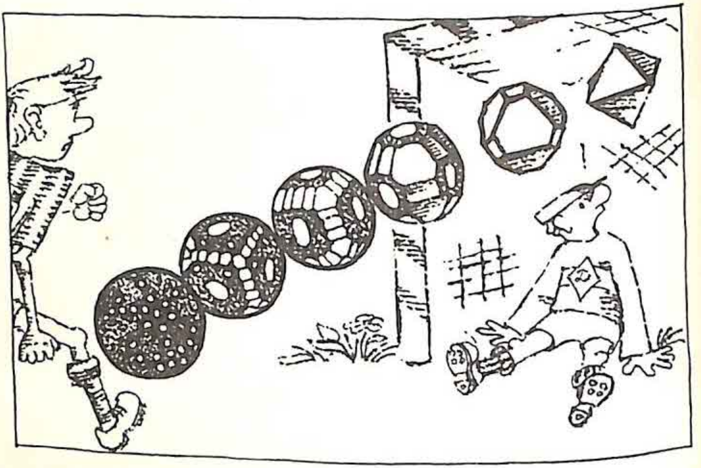

Figure 4.7

as we say, best-developed, ones. It is a principle that a grown crystal is always bounded by its slowest-growing faces.

This is especially clear from the illustration at the right in Figure 4.6. Here a formless fragment acquires the same shape as the other crystals precisely owing to the anisotropy of growth rates. Quite definite faces develop at the expense of others more and more resolutely, and impart the shape, or habit, to the crystal that is inherent in all specimens of this substance.

Very handsome intermediate shapes are observed if a sphere is taken as a seed crystal and the solution is alternately cooled slightly and then heated slightly. Upon being heated the solution becomes undersaturated and the seed crystal is partly dissolved. Cooling leads to oversaturation of the solution and growth of the seed crystal. But the molecules attach themselves differently than they were before being dissolved, seeming to give

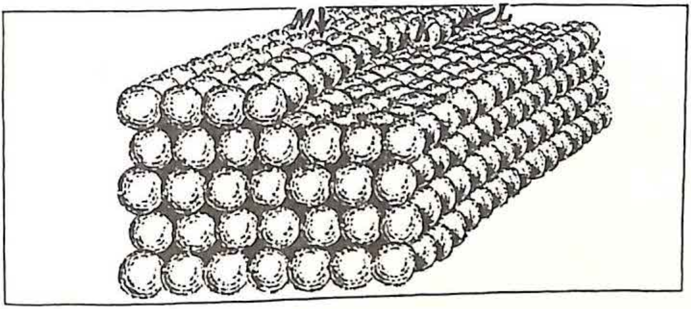

Figure 4.8

preference to certain locations. The substance is thus transferred from certain parts of the sphere to other parts.

First small circular faces appear on the surface of the sphere. These circles gradually increase in size and, contacting one another, merge along straight edges. The sphere is converted into a polyhedron. Then certain faces overtake others in their growth, a part of the faces become smaller and smaller and disappear. Finally, the crystal reaches its characteristic shape, or habit (Figure 4.7).

In observing the growth of a crystal, one of its features may astound us—the seemingly parallel motion of its faces. This implies that the substance separating out of the solution is deposited on the faces in layers, and that a succeeding layer is not started until the preceding one is completed.

Illustrated in Figure 4.8 is an "incompleted" packing arrangement of atoms. In which of the positions indicated by letters is a new atom, attaching itself to the crystal, most likely to remain secured? Without doubt, in position *K* because here it is subject to attraction by its neighbours from three sides. In position *L* the new atom is attracted from two sides, and in position *M* from only one. This is why a row is first completed, then a whole layer and finally a new layer is started.

In many cases, crystals are formed from a molten mass, or melt. This takes place on an immense scale in nature; basalts, granites and other kinds of igneous rocks were formed of fiery magma.

Let us heat some kind of crystalline substance, for example, rock salt. Up to a temperature of 804 °C, the salt crystals change very slightly; they only expand negligibly, but the substance remains a solid. A thermometer placed in the vessel with the substance indicates a continuous increase in temperature during heating. At 804 °C, we discover two new interrelated phenomena: the substance begins to melt and the temperature ceases to increase any further. Until all of the substance is converted into a liquid, the temperature remains unchanged. A further increase in temperature indicates that we are heating the liquid. All crystalline substances have a definite melting point. Ice melts at 0 °C, iron at 1527 °C and mercury at 39 °C below zero, etc.

As we already know, in each small crystal the atoms or molecules of the substance form an ordered packing arrangement and have small vibrations about their mean positions. As the body is heated, the velocity of the vibrating particles increases together with the amplitude. This increase in the velocity of motion of particles as the temperature is raised is one of the basic laws of nature and concerns matter in any state—solid, liquid or gaseous.

When the temperature of the crystal has reached a definite, sufficiently high value, the vibration of its particles becomes so violent that an accurate arrangement of the particles is no longer possible; the crystal melts. As melting begins, the heat supplied no longer increases the velocity of motion of the particles, it is employed to break up the crystal lattice. This is why the temperature remains constant until all of the substance melts. Subsequent heating increases the velocity of the particles of liquid.

In our case of crystallization from a melt, called freezing, all the phenomena described above occur in the reverse order: as the liquid is cooled, the chaotic motion of its particles slows down. When a definite, sufficiently low temperature has been reached, the velocity of the particles is so low that some of them begin to align themselves with others, forming a crystal nucleus. Until the whole substance has frozen, or solidified, the temperature remains constant. As a rule, this temperature is the same as the melting point.

Unless special measures are taken, freezing begins in the melt simultaneously at many places. The small crystals begin to grow as regular polyhedrons characteristic of the given substance in exactly the same way as we described above. Such free growth soon ends, however, because the growing small crystals run into one another, with further growth ceasing at the points of contact. This imparts a granular structure to the solidified body. Each grain is a small crystal that was unable to assume its regular shape.

Depending on many factors, and primarily on the cooling rate, a solid can consist of coarser or finer grains. The lower the cooling rate, the coarser the grains. The grain size of crystalline bodies ranges from a millionth of a centimetre to several millimetres. In the majority of cases, the granular crystalline structure can be observed under a microscope. Most solids have such a fine-crystalline structure.

The freezing of metals is a process of vital interest to engineering. Physicists have investigated in exceptionally great detail the phenomena occurring when molten metal is poured into a mould in a foundry and solidifies.

Mostly small tree-like crystals, called *dendrites*, grow in a molten metal when it is cooled. Sometimes the den-

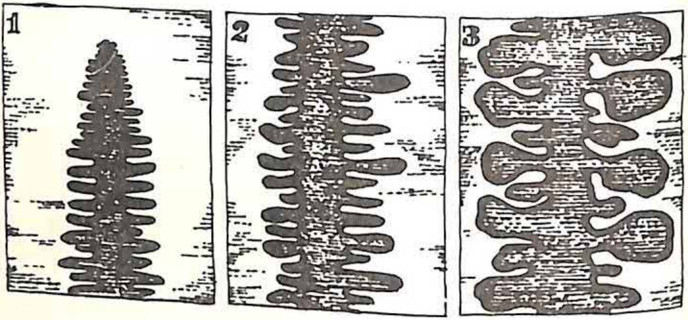

Figure 4.9

drites are oriented at random, and sometimes they are parallel to one another.

The stages of growth of a single dendrite are illustrated in Figure 4.9. Under such circumstances, the dendrite can become overgrown, occupying all the space between its branches, before encountering another dendrite in the melt. Then we find no dendrites in the solidified casting. But events can develop differently: dendrites may meet and grow into one another (with the branches of one filling the spaces between the branches of another) while they are still in an early stage of growth.

Hence, we may obtain castings whose grains (shown in Figure 2.22) have very different structures. The properties of metals depend essentially upon this structure. We can control the behaviour of a metal in solidifying by varying the cooling rate and the system of heat disposal from the mould.

If we wish to grow a large single crystal, we must take steps to have the crystal grow in one place. But if several crystals have already started growing, then in any case we must take steps to make the conditions for growth favourable for only one of them.

Here, for example, is what one does in growing crystals of fusible metals. The metal is melted in a glass test tube with a drawn-out bottom. The test tube, suspended on a thread inside a vertical cylindrical oven, is slowly lowered. The drawn-out bottom gradually leaves the oven and cools off. Crystallization begins. At first, several tiny crystals are formed, but those which grow sideways come up against the test tube wall and their growth is slowed down. Only the crystal which grows along the axis of the test tube, i.e. into the heart of the melt, proves to be in favourable conditions. As the test tube is lowered, new portions of the melt coming into a low-temperature region will "feed" this unique crystal. Therefore, of all the tiny crystals, it alone will survive; as the test tube is lowered, it continues to grow along its axis. At last, all of the melted metal hardens in the form of a single crystal.

The same idea underlies the growing of refractory crystals of ruby. Fine ruby powder is poured in a stream through a flame. As a result, the particles of powder melt; tiny droplets fall on a refractory support of very small area forming a mass of crystals. During the further fall of droplets on the support, all the tiny crystals will grow, but once again only the one which is in the most advantageous position for "receiving" the falling drops will develop.

But what are large crystals needed for?

Industry and science are often in need of large single crystals. Of great significance for technology are crystals of Seignette salt and quartz possessing the remarkable property of transforming mechanical action (for example, pressure) into voltage.

The optical industry needs large crystals of calcite, rock salt, fluorite, etc.

Crystals of ruby, sapphire and certain other precious stones are needed for the watchmaking. The reason for this is that individual movable parts of ordinary watches perform up to 20 000 oscillations per hour. This makes unusually heavy demands on the quality of the tips of the axes and the bearings. The wear will be least when ruby or sapphire serves as the bearing for the tip of an axis of 0.07-0.15 mm in diameter. Artificial crystals of these substances are very durable and are worn out very little by steel. It is remarkable that artificial stones prove to be better for this purpose than the same natural stones.

Of greatest significance in industry, however, is the growing of semiconductor (silicon) monocrystals. The communications-electronics of today is inconceivable without these crystals.

Influence of Pressure on Melting Point

If the pressure is changed, the melting point will also change. We came across such a regularity when dealing with boiling. The greater the pressure, the higher the boiling point. As a rule, this is also true for melting. However, there are a small number of substances which behave anomalously: their melting points decrease with an increase in pressure.

The fact of the matter is that the vast majority of solids are denser than their liquids. The exceptions to this rule are precisely those substances whose melting points change somewhat unusually with a change in pressure, for example, water. Ice is lighter than water, and the melting point of ice is lowered by an increase in pressure.

Compression facilitates the formation of the denser state. If the solid is denser than the liquid, then compression aids solidification and hinders melting. But if melting is obstructed by compression, this means that the substance remains solid, whereas previously it would have melted at this temperature, i.e. the melting point rises with an increase in pressure. In an anomalous case, the liquid is denser than the solid, and so the pressure helps to form the liquid, i.e. lowers the melting point.

The influence of the pressure on the melting point is much less than the analogous effect for boiling. An increase in pressure of more than 100 kgf/cm^2 lowers the melting point of ice by 1 °C.

Why is it that skates glide on ice but do not slide on a highly polished parquet floor that is just as smooth as ice? The only feasible explanation, evidently, is the formation of water which lubricates the runners of the skates. But the pressure exerted by the runner does not in any case exceed 100 kgf/cm^2, and this would not seem to lower the melting point of the ice sufficiently so that it melts under the runners. All I can say to eliminate this contradiction is the following: skates with blunt runners slide very poorly on ice. The runners must be ground so that they cut the ice. Then only the sharp edges of the runners contact the ice, exerting a pressure of tens of thousands of atmospheres and the ice *does* melt.

Evaporation of Solids

When we say that a substance is evaporating, it is usually implied that a liquid is evaporating. But solids can also evaporate. The evaporation of solids is sometimes called *sublimation*.

Naphthalene, for example, is an evaporating solid. Naphthalene melts at 80 °C, but evaporates at room temperature. It is precisely this property of naphthalene which enables it to be used for the extermination of moths. A fur coat powdered with naphthalene will become saturated with naphthalene vapours, creating an atmosphere which moths cannot bear. Every solid with an odour sublimes to a significant degree. In fact, the odour is created by the molecules which have broken away from the substance and reached our nose. However, the cases

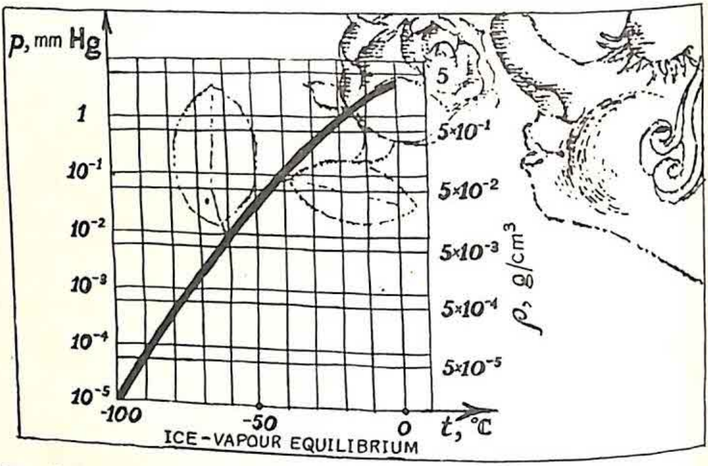

Figure 4.10

where a substance sublimes to an insignificant degree, sometimes to a degree that cannot be detected by even the most careful investigation, are more frequent. In principle, any solid (yes, any, even iron or copper) evaporates. If we do not detect sublimation, this merely means that the saturated vapour density is very negligible.

The saturated vapour density in equilibrium with the solid grows rapidly with temperature (Figure 4.10). It is possible to convince oneself that a number of substances having sharp odours at room temperature lose them at low temperatures.

In most cases it is impossible to considerably increase the saturated vapour density of a solid for a simple reason—the substance will melt beforehand.

Ice also evaporates. This is well known to housewives who hang up their wash to dry during a frost. At first the water will freeze, but then the ice evaporates and the wash turns out to be dry.

Triple Point

Thus, there are conditions under which a vapour, a liquid and a crystal can exist pairwise in equilibrium.

Can all three states be in equilibrium? Such a point exists on the pressure-temperature diagram, it is called the *triple point*. Where is it located?

If ice floating on water is placed in a closed vessel at a temperature of zero degrees, water (and "ice") vapour will start entering the free space. At a pressure of 4.6 mm Hg, evaporation will cease and saturation will set in. Now the three phases, ice, water and vapour, will be in a state of equilibrium. This is precisely the triple point.

The relationships between the various states are graphically and clearly shown by the diagram for water depicted in Figure 4.11. Such a diagram can be constructed for any substance.

We are acquainted with the curves in the diagram — they are the equilibrium curves for ice and water vapour, ice and water, and water and water vapour. As is customary, the pressure is plotted along the vertical axis, and the temperature along the horizontal.

The three curves intersect in the triple point and divide the diagram into three regions—the living spaces for ice, water and water vapour.

A phase diagram is a concise handbook. Its aim is to answer questions as to what state of a substance is stable at a given pressure and a given temperature.

If water or water vapour is placed under the conditions of the "left-hand region", it will turn into ice. If water or ice is introduced into the "lower region", water vapour will be obtained. In the "right-hand region", water vapour will condense and ice will melt.

The phase diagram permits one to immediately say what will happen to a substance when it is heated or compressed. Heating at a constant pressure will be depicted

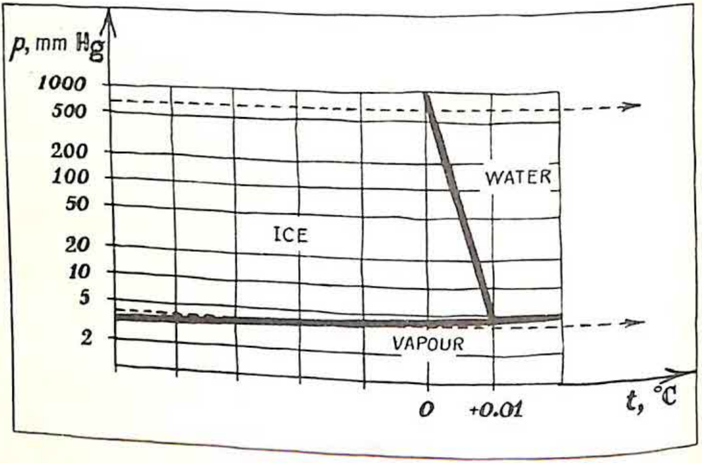

Figure 4.11

on the diagram by a horizontal line. The point depicting the phase of the substance will move from left to right along this line.

Two such lines are depicted in the figure, one of which is heating under standard pressure. This line lies above the triple point. Therefore, it will first intersect the melting point curve, and then, beyond the bounds of the diagram, the evaporation curve too. Under standard pressure, ice melts at a temperature of 0 °C, while the water so formed will boil at 100 °C.

The situation will be different for ice heated under a very low pressure, say, a bit less than 5 mm Hg. The heating process is depicted by a line passing beneath the triple point. The melting and boiling point curves do not intersect this line. Under such a negligible pressure, heating leads to a direct transition of ice to water vapour.

In Figure 4.12, this same diagram shows what an interesting phenomenon will occur when water vapour in

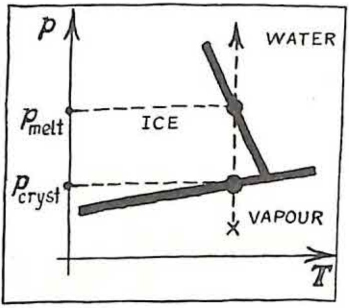

Figure 4.12

the state marked on the figure by a cross is compressed. The vapour will first be converted into ice, which will then melt. The diagram enables us to say at once at what pressure the growth of crystals will begin and when the melting takes place.

The phase diagrams for all substances resemble each other. Significant, from the everyday point of view, differences arise because the location of the triple point on the diagram can be most diverse for various substances.

After all, we exist under conditions which are close to "standard", i.e. in the first place, under a pressure close to one atmosphere. The way in which the triple point of a substance is located with respect to the standard pressure line is very important for us.

If the pressure at the triple point is less than atmospheric, then for us, living under "standard" conditions, the substance will be one of those that melt. As the temperature rises, it will first be transformed into a liquid, which will then boil.

In the opposite case, when the pressure at the triple point is higher than atmospheric, we will not see any liquid when the substance is heated, since the solid will be converted directly into a vapour. This is how "dry ice" behaves, which is very convenient for ice cream vendors.

They can distribute pieces of "dry ice" among the portions of ice cream without worrying that the ice cream will become wet as a result. "Dry ice" is solid carbon dioxide, CO_2. Its triple point lies at 73 atm. Therefore, when solid CO_2 is heated, the point depicting its state will move along a horizontal line intersecting only the evaporation curve of the solid (just as for ordinary ice at a pressure of about 5 mm Hg).

We have already explained how one degree of temperature on the Kelvin scale, or kelvin (as we are now required to call it by the SI system), is determined. The point of the discussion there was the principle involved in determining temperatures. But not all metrological institutes have ideal gas thermometers at their disposal. Therefore, a temperature scale is usually established with the aid of points of equilibrium, fixed by nature, between various states of substances.

Of especial significance in this matter is the triple point of water. A kelvin is determined today as 1/273.16 of the thermodynamic temperature of the triple point of water. The triple point of oxygen is taken equal to 54.361 K. The freezing point of gold is equal to 1337.58 K. Using these datum points we can readily graduate any thermometer.

The Same Atoms but Different Crystals

The dull, soft graphite with which we write and the bright, transparent, hard, cutting glass, diamond are made of one and the same atoms — atoms of carbon. Why then are there such differences between the properties of these two substances identical in composition?

Recall the lattice of flaky graphite each of whose atoms has three nearest neighbours, and the lattice of diamond whose atoms have four nearest neighbours. It is clearly evident from this example how the properties of crystals are determined by the mutual distribution of their atoms. Fireproof crucibles, withstanding temperatures up to two or three thousand degrees, are made of graphite, but diamond burns at temperatures above 700 °C; the specific gravity of diamond is 3.5, of graphite 2.3; graphite conducts electricity, but diamond does not, etc.

This property of forming various crystals is possessed not only by carbon. Almost every chemical element, and not only element but also any chemical substance, can exist in several varieties. Six varieties of ice, nine varieties of sulphur and four varieties of iron are known.

In discussing a phase diagram, we did not speak of the various types of crystals, but drew a single region for the solid. But for a great many substances, this region is divided up into sections each of which corresponds to a definite "sort" of solid body or, as one says, a definite solid phase (a definite crystal modification).

Each crystal phase has its own region of stable state bounded by definite intervals of pressure and temperature. The laws of transformation of one crystal variety into another are the same as the laws of melting and evaporation.

Given any pressure, one can find a temperature at which both types of crystals will peacefully coexist. If we raise the temperature, a crystal of one form will be converted into a crystal of the second. If we lower the temperature, the reverse transformation will take place.

In order to convert red sulphur into yellow under standard pressure, a temperature below 110 °C is needed. Above this temperature, right up to the melting point, the order of the distribution of atoms characteristic of red sulphur is stable. When the temperature falls, the oscillations of the atoms decrease, and, beginning with 110 °C, nature finds a more convenient order for the distribution of the atoms. A transformation of one crystal into another occurs.

Nobody has thought of names for the six different ices. This is what one says: ice one, ice two, . . ., ice seven. How come seven if there are only six varieties? The reason is that repeated experiments have failed to detect ice four.

If water is compressed at a temperature of about zero, ice five will be formed at a pressure of about 2000 atm, and ice six at a pressure of about 6000 atm.

Ice two and ice three are stable at temperatures below zero degrees centigrade.

Ice seven is a hot ice; it appears when hot water is subjected to a pressure of about 20 000 atm.

All ices, except the ordinary one, are heavier than water. Ice obtained under standard conditions behaves anomalously; on the contrary, ice obtained under conditions differing from the norm behaves normally.

We say that each crystal modification is characterized by a definite region of existence. But if so, how can graphite and diamond possibly exist under identical conditions?

Such "lawlessness" is found very often in the world of crystals. The ability to live under "alien" conditions is almost a rule for crystals. While one must turn to various tricks in order to transfer a vapour or a liquid to alien regions of existence, a crystal, on the contrary, can almost never be forced to stay within the frontiers marked off for it by nature.

The superheating and supercooling of crystals are explained by the difficulty in transforming one order into another under conditions of extreme overcrowding. Yellow sulphur should be transformed into red at 95.5 °C. During a more or less rapid heating, we "slip past" this transformation point and drive it up to 113° C.

The true transformation point is most easily detected when different crystals are in contact. If we put one up close against the other and maintain a temperature of

96 °C, the yellow sulphur will be eaten up by the red, but the yellow will swallow the red at 95 °C. Unlike a "crystal-liquid" transition, a "crystal-crystal" transformation is ordinarily delayed during superheating, just as during supercooling.

In certain cases, we come across states of a substance which are supposed to exist at entirely different temperatures.

White tin must turn into grey when the temperature falls to +13 °C. We ordinarily use things made of white tin and know that nothing will happen to them in winter. White tin withstands supercooling of 20-30 degrees perfectly well. However, under conditions of a severe winter, white tin is transformed into grey. The lack of knowledge of this fact was one of the circumstances destroying Scott's expedition to the South Pole (1912). The liquid fuel taken along by the expedition was kept in vessels soldered with tin. During severe frosts, the white tin was transformed into a grey powder, the vessels came unsoldered and the fuel was spilt. Not without reason is the appearance of grey spots on white tin called tin plague.

Just as in the case of sulphur, white tin can be converted into grey at a temperature a bit lower than 13 °C, if a tiny grain of the grey variety falls on a tin object.

The existence of several varieties of one and the same substance and the delays in their mutual transformations have great significance for technology.

At room temperature, iron atoms form a body-centred cubic lattice, occupying the vertices and centre of each cube. Every atom has 8 neighbours. At a high temperature, iron atoms form a denser "packing"—each atom has 12 neighbours. Iron with 8 neighbours per atom is soft; iron with 12 neighbours per atom is hard. It turns out that it is possible to obtain iron of the latter type at room temperature. The method whereby this is done, hardening, is widely applied in metallurgy.

Hardening is accomplished quite simply—the metallic object is made red-hot and then thrown into water or oil. Cooling occurs so rapidly that there is no time for the transformation of the structure stable at a high temperature to take place. Consequently, the high-temperature structure will exist indefinitely under conditions unnatural to it; recrystallization into a stable structure occurs so slowly that it is practically unnoticeable.

In speaking of the hardening of iron, we were not quite exact. Steel, i.e. iron containing a fraction of a per cent of carbon, is hardened. The presence of very small admixtures of carbon delays the transformation of hard iron into soft and permits the hardening to be carried out. As fro completely pure iron, one cannot succeed in hardening it—there is time for the conyersion of its structure to take place even during the most rapid cooling.

Depending on the form of the phase diagram, one or another transformation is achieved by changing the pressure or the temperature.

Many transformations of a crystal into a crystal are observed during a change of only the pressure. Black phosphorus was obtained in this way.

Graphite was able to be converted into diamond only by simultaneously using both high temperature and pressure. The phase diagram for carbon is depicted in Figure 4.13. At pressures below ten thousand atmospheres and at temperatures less than 4000 K, graphite is the stable modification. Therefore, diamond exists under "alien" conditions, and so it can be transformed into graphite without particular difficulty. But the inverse problem is of practical interest. We cannot succeed in carrying out a transformation of graphite into diamond by only raising the pressure. A phase transformation in the solid state apparently goes too slowly. The form of the phase diagram suggests the correct solution: increase the pressure and heat the graphite simultaneously. We then obtain (upper

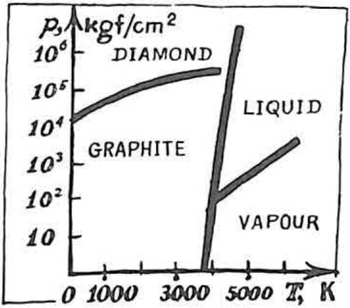

Figure 4.13

right-hand corner of the diagram) melted carbon. Cooling it at a high pressure, we should enter the region of diamond.

The practical possibility of such a process was proved in 1955, and at the present time the problem is considered to be solved from technological point of view.

An Amazing Liquid

If we lower the temperature of a body, sooner or later it will solidify and acquire a crystal structure. Moreover, it makes no difference at what pressure the cooling takes place. This circumstance seems perfectly natural and understandable from the point of view of the physical laws with which we have already become acquainted. In fact, by lowering the temperature, we decrease the intensity of the thermal motion. When the motion of molecules becomes so weak that it has already ceased to interfere with the forces of interaction between them, the molecules will line up in an accurate order—will form crystals. A further cooling will take away from the molecules all the energy of their motion, and at absolute zero, a substance should exist in the form of molecules at rest distributed in a regular lattice.

Experiments show that all substances behave in this manner. All but one unique substance: this "freak" is helium. We have already informed the reader of certain facts concerning helium. It holds the record for the value of its critical temperature. Not a single substance has its critical temperature lower than 4.3 K. However, this record by itself does not imply anything amazing. Something else is startling: cooling helium below the critical temperature and practically reaching absolute zero, we will not obtain solid helium. Helium remains liquid even at absolute zero.

The behaviour of helium is completely unexplainable from the point of view of the laws of motion presented by us, and is one of the signs of the limited validity of the laws of nature which seemed universal.

If a substance is liquid, its atoms are in motion. But in cooling it down to absolute zero, we have taken all the energy of motion away from it. We have to admit that helium has an energy of motion which cannot be taken away. This conclusion is incompatible with the mechanics which we have been studying so far. According to the mechanics we learned, the motion of a body can always be slowed down to a complete halt by taking away all its kinetic energy; the motion of molecules can also be stopped in exactly the same way by taking energy away from them during collisions with the walls of the vessel being cooled. Such a mechanics will obviously not do for helium.

The "strange" behaviour of helium is an indication of a fact of enormous importance. This is the first time that we have come up against the impossibility of applying in the world of atoms the basic laws of mechanics established by means of a direct investigation of the motion of visible bodies—laws which seemed to constitute a firm foundation for physics.

The fact that helium "refuses" to crystallize at absolute

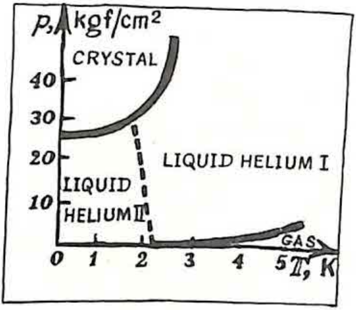

Figure 4.14

zero is by no means possible to reconcile with the mechanics which we have been studying until now. The contradiction which we have come across for the first time, that atoms do not obey the laws of mechanics, is merely the first link in a chain of sharper and more glaring contradictions in physics.

These contradictions have led to the necessity of revising the foundations of the mechanics of atomic motion. This revision is very profound and has led to a change in our entire understanding of nature.

The necessity for a radical revision of the mechanics of atomic motion does not imply that we must give up the laws of mechanics we have studied as a bad job. It would have been unfair to make the reader study unnecessary things. The old mechanics is completely valid in the world of large bodies. This is already enough for us to regard the corresponding chapters of physics with complete respect. However, it is also important that a number of laws of the "old" mechanics pass over without change into the "new" mechanics. Among them, in particular, is the law of conservation of energy.

The presence of "inalienable" energy at absolute zero is not a special property of helium. It turns out that all substances have "zero" energy. Only for helium does this energy prove sufficient to prevent the atoms from forming a regular crystal lattice.

One must not think that helium cannot occur in a crystalline state. It is merely necessary to raise the pressure to approximately 25 atm in order to crystallize helium. Cooling carried out above this pressure leads to the formation of solid crystalline helium with perfectly ordinary properties. Helium forms a face-centred cubic lattice.

The phase diagram for helium is shown in Figure 4.14. It differs greatly from the diagrams of all other substances in the absence of a triple point. The melting and boiling point curves do not intersect.

5. Solutions

What a Solution Is

If broth is salted and stirred with a spoon, no traces of salt will remain. It should not be thought that the grains of salt are simply not visible to the unaided eye. One will not succeed in detecting the tiny salt crystals in any way, because they have dissolved. If pepper is added to the broth, no solution will be obtained. One can even stir the broth for days on end, but the tiny black grains will not disappear.

But what do we mean when we say that a substance has dissolved? For the atoms or molecules composing it cannot vanish without a trace, can they? Of course not, and they do not vanish. When dissolving, only the grains of a substance, crystals, accumulations of molecules of a single sort disappear. A *dissolution* consists in stirring the particles of a mixture in such a manner that the molecules of one substance are distributed between the molecules of another. A *solution* is the mixture of molecules or atoms of different substances.

A solution can contain various amounts of a solute. The composition of a solution is characterized by its concentration, for example, the ratio of the number of grams of a solute to the number of litres of a solution.

As we add a solute, the concentration of a solution grows but not without bound. Sooner or later the solution will become saturated and will cease "taking in" the solute. The concentration of a saturated solution, i.e. the "limiting" concentration of the solution, is called the *solubility*.

It is possible to dissolve a surprising amount of sugar in hot water. At a temperature of 80 °C, a full glass of water will accept 720 g of sugar with no residue. This saturated solution will be thick and viscous, and is called a sugar syrup by cooks. The figure we just gave for sugar is for a cup which holds 0.2 l. Hence, the concentration of sugar in water at 80 °C is equal to 3600 g/l (which is read "grams per litre").

The solubility of certain substances is highly dependent on the temperature. At room temperature (20 °C), the solubility of sugar in water falls to 2000 g/l. On the contrary, the solubility of salt changes quite insignificantly with a change in temperature.

Sugar and salt dissolve well in water. But naphthalene is practically insoluble in water. Different substances dissolve quite differently in different solvents.

Solutions are used for growing monocrystals. If a small crystal of a solute is suspended in a saturated solution, then as the solvent evaporates, the solute will settle out on the surface of this crystal. Moreover, the molecules will preserve a strict order, and, as a result, the small crystal will be transformed into a large one, remaining a monocrystal.

Solutions of Liquids and Gases

Is it possible to dissolve a liquid in a liquid? Of course, it is. For example, vodka is a solution of alcohol in water (or, if you wish, of water in alcohol—depending on what there is more of). Vodka is a real solution; the molecules of water and alcohol are completely mixed up in it.

However, such a result is not always obtained when two liquids are mixed.

Try adding kerosene to water. No matter how you stir, you will not succeed in obtaining a uniform solution; this is just as hopeless as trying to dissolve pepper in soup.

As soon as you stop stirring, the liquids arrange themselves in layers: the heavier water at the bottom, the lighter kerosene on the top. Kerosene with water and alcohol with water are systems having opposite properties with respect to their solubility.

However, there are also intermediate cases. If we mix ether with water, we shall clearly see two layers in the vessel. At first glance, it might appear that on the top is ether and at the bottom is water. But as a matter of fact, the lower and upper layers are solutions: at the bottom is water in which part of the ether is dissolved (the concentration being 25 grams of ether to a litre of water), while on the top is ether in which there is a noticeable amount of water (60 g/l).

Let us now turn our attention to solutions of gases. It is clear that an unlimited amount of an arbitrary gas will dissolve in any other gas. Two gases always intermingle in such a way that the molecules of one penetrate between the molecules of the other. For gas molecules interact but slightly with each other, and so each gas behaves in the presence of another gas by, in a certain sense, not paying any "attention" to its cohabitant.

Gases can also dissolve in liquids. However, not in arbitrary amounts but in limited ones, not differing in this respect from solids. Moreover, different gases dissolve differently, and these differences can be very great. Immense amounts of ammonia can dissolve in water (about 100 grams to half a glass of cold water), and large amounts of hydrogen sulphide and carbon dioxide. Oxygen and nitrogen are soluble in water in only negligible amounts (0.07 and 0.03 grams per litre of cold water). Therefore, there is a total of only about one-hundredth of a gram of air in a litre of cold water. However, even this small amount plays a large role in life on the Earth, for fish breathe the oxygen of the air dissolved in water.

The greater the pressure of a gas, the more of it will be dissolved in a liquid. If the amount of a dissolved gas is not very great, there is a direct proportionality between it and the pressure of the gas above the surface of the liquid.

Who has not enjoyed a glass of cold soda, so good for quenching one's thirst. It is possible to obtain soda because of the dependence of the amount of a dissolved gas on the pressure. Carbon dioxide is driven into water under pressure (from the cylinders which are in every store where soda is sold). When soda is poured into a glass, the pressure falls to atmospheric and the water gives off the "superfluous" gas in the form of bubbles.

Taking such effects into account, deep-sea divers should not rise rapidly from under the water to the surface. Additional amounts of air dissolve in a diver's blood under the high pressure of deep water. When rising, the pressure falls and air begins separating out in the form of bubbles which can stop up the blood vessels.

Solid Solutions

The word "solution" is applied to liquids in everyday life. However, there also exist solid mixtures whose atoms and molecules are uniformly distributed. But how can one obtain solid solutions? You won't get them with the aid of mortar and pestle. Therefore, we must first turn the substances to be mixed into liquids, that is melt them, then mix the liquids and allow the mixture to solidify. One can also act otherwise, dissolving the two substances which we want to mix in some liquid and then evaporating the solvent. Solid solutions might be obtained by such means. They might be, but they cannot ordinarily be so obtained. Solid solutions are rarities. If a piece of sugar is thrown into salty water, it will dissolve excellently. Evaporate the water; the minutest crystals of salt and sugar will be found at the bottom of the cup. Salt and sugar do not yield solid solutions.

It is possible to melt cadmium and bismuth in a single crucible. After cooling, we can see a mixture of cadmium and bismuth crystals through a microscope. Bismuth and cadmium do not form solid solutions either.

A necessary although not a sufficient condition for the emergence of solid solutions is the affinity of the molecules or atoms of the substances being mixed in form and dimensions. In this case, crystals of one sort are formed when the mixture freezes. The lattice points of each crystal are usually occupied randomly by atoms (molecules) of different sorts.

Alloys of metals of great technological value are frequently solid solutions. The dissolution of a small amount of an admixture can radically change the properties of a metal. A striking illustration of this is the obtaining of one of the most widespread materials in technology—steel, which is a solid solution of small amounts of carbon (of the order of 0.5 of weight per cent, that is one atom of carbon to 40 atoms of iron) in iron, where the atoms of carbon are randomly distributed between the atoms of iron.

Only a small number of carbon atoms dissolve in iron. However, some solid solutions are formed by mixing substances in arbitrary proportions. Alloys of gold and copper can serve as an example. Crystals of gold and copper have lattices of the same type—face-centred cubic. An alloy of copper with gold has the same lattice. An idea of the structure of alloys with an increasing percentage of copper can be obtained by conceptually deleting atoms of gold from the lattice and replacing them by atoms of copper. Moreover, the replacement occurs disorderly, with the copper atoms generally being distributed randomly among the lattice points.

Alloys of copper with gold may be called solutions of replacement, whereas steel is a solution of a different type, a solution of introduction.

In the vast majority of cases, solid solutions do not arise, and, as has been said above, after cooling we can see in the microscope that the substance consists of a mixture of tiny crystals of both substances.

How Solutions Freeze

If a solution of any salt in water is cooled, it will be discovered that the freezing point has been lowered. Zero mark is past, but solidification does not occur. Only at a temperature of several degrees below zero do tiny crystals appear in the liquid. They are tiny crystals of pure ice: salt does not dissolve in solid ice.

The freezing point depends on the concentration of a solution. Increasing the concentration of a solution, we shall lower its freezing point. A saturated solution has the lowest freezing point. The decrease in the freezing point of a solution is not at all small: thus, the saturated solution of sodium chloride in water freezes at —21 °C. With the aid of other salts, we can achieve an even greater fall in temperature; calcium chloride, for example, enables us to bring the freezing point of a solution down to —55 °C.

Let us now consider how the process of freezing takes place. After the first tiny crystals of ice have fallen out of a solution, the concentration of the solution increases. Now the relative number of alien molecules grows, the obstacles to the process of the crystallization of water also increase and the freezing point falls. If we do not further lower the temperature, then crystallization will cease. With a further lowering of temperature, tiny crystals of water (the solvent) continue separating out. Finally, the solution becomes saturated. A further enrichment of the solution by the solute becomes impossible, and the solution solidifies at once; moreover, if we look at the frozen mixture through a microscope, we can see that it consists of tiny crystals of ice and tiny crystals of salt.

Consequently, the freezing of a solution is unlike that of a simple liquid. The process of freezing is spread out over a wide temperature interval.

What will happen if we pour salt on some frozen surface? The answer to this question is well known to yard men—as soon as salt comes in contact with ice, the ice begins melting. In order that this phenomenon take place, it is necessary, of course, that the freezing point of a saturated salt solution be lower than the temperature of the air. If this condition is met, the mixture of ice and salt is in an alien phase region, namely, in the region of stable existence. Therefore, the mixture of ice with salt will turn into a solution, i.e. the ice will melt and the salt will dissolve in the water so formed. Finally, either all the ice will melt or else a solution of such a concentration will be formed that its freezing point will be equal to the temperature of the surroundings.

Suppose that a yard whose area is 100 m^2 is covered by a 1-cm layer of ice—this is quite a bit of ice, about one ton. Let us calculate how much salt is needed to melt this ice if the temperature is —3 °C. For such a freezing (melting) point the concentration of a salt solution must be 45 g/l. Approximately one litre of water corresponds to one kilogram of ice. Hence, in order to melt one ton of ice at —3 °C, 45 kg of salt are needed. A much smaller amount is used in practice since one does not seek the complete melting of all the ice.

Ice melts when mixed with salt, and salt dissolves in water. But heat is required for melting, and the ice takes it from its surroundings. Therefore, the addition of salt to ice leads to a decrease in temperature.

We are now in the habit of buying ice cream, but it was previously made at home. In this connection, a mixture of ice and salt played the role of a coolant.

Boiling of Solutions

Boiling of solutions has a lot in common with their freezing.

The presence of a solute hinders crystallization. For the very same reasons, a solute also hinders boiling. In both cases it is as though alien molecules were fighting to retain a solution which is as diluted as possible. In other words, the alien molecules stabilize the state of the basic substance (i.e. facilitate its existence), which can dissolve them.

Therefore, alien molecules impede the crystallization of a liquid, and so lower the freezing point. In exactly the same way, alien molecules impede the boiling of a liquid, and so raise its boiling point.

It is curious that within certain limits of concentration (for not very concentrated solutions), neither the lowering of the freezing point of a solution nor the raising of its boiling point depends in the least on the properties of the solute but is determined only by the number of its molecules. This interesting circumstance is used for the determination of the molecular mass of soluble substances. This is done with the aid of a remarkable formula (we cannot give it here), which relates the change in the freezing or boiling point to the number of molecules in a unit volume of a solution (and to the heat of fusion or boiling).

The boiling point of water is raised one-third as much as its freezing point is lowered. Thus, sea water containing approximately 3.5% of salt has a boiling point of 100.6 °C, while its freezing point is lowered by 2 °C.

If one liquid boils at a higher temperature than another, then (at the same temperature) its vapour pressure is lower. Hence, the vapour pressure of a solution is less than that of the pure solvent. One can judge the difference on the basis of the following values: the vapour pressure at 20 °C equals 17.5 mm Hg and the vapour pressure of a saturated solution of sodium chloride at the same temperature is 13.2 mm Hg.

Vapour with a pressure of 15 mm Hg, unsaturated for water, will be supersaturated for a saturated salt solution. In the presence of such a solution, the vapour starts condensing and uniting with the solution. Of course, not only a salt solution but also powdered salt will take water vapour out of the air. In fact, the very first drop of water falling on the salt will dissolve it and create a saturated solution.

The absorption of water vapour from the air by salt leads to the salt's becoming moist. This is well known to hosts and affords them grief. But this decrease in vapour pressure over a solution can also be of benefit: it is used for drying air in laboratory practice. Air is passed through calcium chloride, which is the record holder in taking moisture out of the air. While a saturated solution of sodium chloride has a vapour pressure of 13.2 mm Hg, that of calcium chloride is 5.6 mm Hg. The vapour pressure will fall to this value when it is passed through a sufficient amount of calcium chloride (1 kg of which "has room for" approximately 1 kg of water). This is a negligible humidity, and such air may be regarded as dry.

How Liquids Are Freed of Admixtures

Distillation is one of the most important means of freeing liquids of admixtures. The liquid is boiled and the vapour is sent into a refrigerator. When cooled, the vapour turns into a liquid once more, but this liquid will be purer than the initial one.

It is easy to get rid of solids dissolved in a liquid with the aid of distillation. Molecules of such substances are practically absent in water vapour. Distilled water is obtained in this way—completely tasteless pure water devoid of mineral admixtures.

However, using evaporation, we can also get rid of liquid admixtures and separate a mixture consisting of two or more liquids. In this connection, we make use of the fact that two liquids forming a mixture do not boil with the same "ease".

Let us see how a mixture of two liquids, for example, of water and ethyl alcohol, taken in equal amounts (100 proof vodka), will behave when boiled.

Under standard pressure, water boils at 100 °C and alcohol at 78 °C. The mixture we are dealing with will boil at the intermediate temperature of 81.2 °C. Alcohol boils more easily, so its vapour pressure is greater, and for an initial fifty-per cent composition of the mixture, the first portion of vapour will contain 80% alcohol.

We can draw off the portion of vapour so obtained into a refrigerator and obtain a liquid enriched by alcohol. This process can be further repeated. However, it is clear that such a method is not practical, for with each successive distillation less and less substance will be obtained. In order that there be no such loss, so-called fractionating (i.e. purifying) columns are applied for the purpose of cleaning a liquid.

The idea behind the structure of this interesting apparatus consists in the following. Imagine a vertical column whose lower part contains a liquid mixture. Heat is supplied below the column and cooling is carried out above it. The vapour formed by boiling rises to the top and condenses; the resulting liquid flows down. For a fixed heat supply from below and heat removal from above, the countercurrents of vapour, going up, and liquid, flowing down, are established in the closed column.

Let us fix our attention on some horizontal cross-section of the column. The liquid passes downwards, and the vapour upwards, through this cross-section; moreover, none of the substances composing the liquid mixture stays behind. If we are dealing with a column containing a mixture of alcohol and water, the amount of alcohol passing upwards and downwards, just as the amount of water passing upwards and downwards, will be equal. Since the liquid is going down and the vapour is coming up, this means that the compositions of the liquid and of the vapour are identical at any height in the column.

As has been just explained, the equilibrium of the liquid and the vapour of a mixture of two substances requires, on the contrary, a difference between the compositions of these phases. Therefore, the conversion of liquid into vapour, and of vapour into liquid, takes place at any height in the column. Moreover, the high-boiling component condenses and the low-boiling component passes from the liquid to the vapour.

Consequently, it is as though the rising vapour were taking away the low-boiling component and the downflowing liquid were continually being enriched by the high-boiling component. The composition of the mixture will become different at each height: the higher the mixture, the greater the percentage of the low-boiling component. In the ideal case, a pure layer of the low-boiling component will be on the top and a pure layer of the high-boiling component will be at the bottom.

The substances should now be drawn off, only as slowly as possible, in order that the ideal picture just outlined not be disturbed, the low-boiling one from the top, and the high-boiling one from the bottom.

In order to carry out the separation, or rectification, in practice, we must make it possible for the countercurrents of liquid and vapour to thoroughly mix. To this end, the currents of liquid and vapour are delayed with the aid of plates distributed one above the other and connected by means of overflow pipes. The liquid can flow down to a lower level from an overfilled plate. The rising vapour (0.3-1 m/s) forces its way through a thin layer of liquid. The diagram of a column is shown in Figure 5.1.

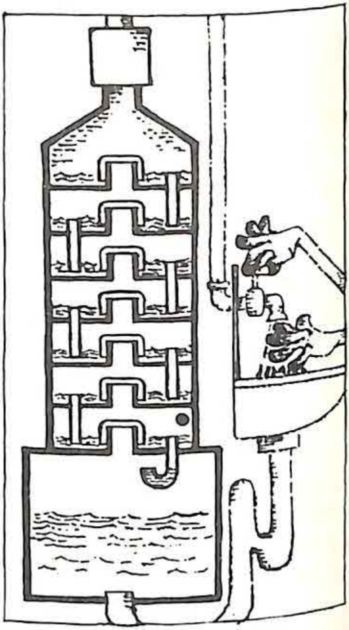

Figure 5.1

One does not always succeed in purifying a liquid completely. Certain mixtures possess an "unpleasant" property: for a definite composition, the ratio of the components of the evaporating molecules is the same as that in the liquid mixture. In this case, of course, a further purification by means of the method described becomes impossible. Such is the mixture containing 96% alcohol and 4% water: it yields a vapour of the same composition. Consequently, 96% alcohol is the best that can be obtained by the evaporation method.

Rectification (or distillation) of liquids is an important process in chemical technology. For example, gasoline is obtained from oil with the aid of rectification.

It is a curious fact that rectification is the cheapest method of obtaining oxygen. For this, of course, one must change air to the liquid phase beforehand, after which one can separate it into almost pure nitrogen and oxygen by means of rectification.

Purification of Solids

On a phial containing a chemical substance alongside of the chemical name one can see, as a rule, the following notation: "pure", "pure for analysis" or "spectroscopically pure". They are used to mark the degree of purity of a substance: "pure" means a rather slight degree of purity—there may possibly be an admixture of the order of 1% in the substance; "pure for analysis" means that admixtures constitute not more than several tenths of a per cent of the substance; "spectroscopically pure" is not easy to obtain, since spectral analysis detects an admixture of several thousandths of a per cent. The inscription "spectroscopically pure" permits us to be confident that the purity of the substance is characterized by at least "four nines", i.e. that the content of the basic substance is not less than 99.99%.

The need for pure solids is quite great. Admixtures of several thousandths of a per cent can change many physical properties, and in one special problem of exceptional interest to modern technology, namely the problem of obtaining semiconductors, technologists require a purity of seven nines. This means that one unnecessary atom among ten million necessary ones prevents us from solving engineering problems! We take recourse in special methods for obtaining such ultrapure materials.

Ultrapure germanium and silicon (these are the main representatives of semiconductors) can be obtained by slowly drawing out a growing crystal from a melt. A rod on whose tip a seed crystal is attached is brought to the surface of melted silicon (or germanium). We then begin slowly raising the rod; the crystal coming out of the melt is made up of the atoms of the basic substance, while the atoms of the admixture remain in the melt.

The method of so-called zone refining has been applied more widely. A rod of arbitrary length and several millimetres in diameter is made out of the material being purified. A small cylindrical oven is placed alongside the rod enveloping it. The temperature in the oven is high enough for melting, and the part of the metal which is inside the oven melts. Therefore, a small zone of melted metal moves along the rod.

The atoms of an admixture usually dissolve much more easily in a liquid than in a solid. Consequently, at the boundary of the melted zone, the atoms of admixture pass from solid parts to the melted zone and do not pass back. It is as though the moving melted zone were dragging off the atoms of the admixture together with the melt. The oven is turned off during the reverse motion, and the operation of pulling the melted zone past the rod of metal is repeated many times. After a sufficient number of cycles, it only remains to saw off the polluted end of the rod. Ultrapure materials are obtained in a vacuum or in an atmosphere of inert gas.

When there is a large fraction of alien atoms, purification is carried out by other methods, the zone melting and pulling a crystal out of a melt being applied only for the final purification of the material.

Adsorption

Gases rarely dissolve in solids, i.e. rarely penetrate crystals. But there exists a different kind of absorption of gases by solids. Molecules of a gas accumulate on the surface of a solid body—this peculiar adherence is called *adsorption**. Thus, adsorption occurs when molecules cannot penetrate within a body, but successfully stick to its surface.

To be adsorbed means to be absorbed by a surface. But can such a phenomenon really play a significant role? In fact, a layer one molecule thick, even on a very large object, will weigh a negligible fraction of a gram.

Let us perform the appropriate calculations. The area of a small molecule is about 10 Å^2, i.e. 10^{-15} cm^2. Hence, 10^{15} molecules will fit into a square centimetre. That many molecules, say, of water, do not weigh much: 3×10^{-8} g. Even in a square metre, there will be room for only 0.0003 g of water.

More noticeable amounts of a substance will form on surface areas of hundreds of square metres. There is as much as 0.03 g of water (10^{21} molecules) per 100 m^2.

But do we come across such sizable surface areas in our laboratory practice? However, it is not hard to grasp that sometimes very small bodies, fitting onto the tip of a teaspoon, have enormous areas of hundreds of square metres.

A cube whose edges are 1 cm long has a surface area of 6 cm^2. Let us cut up such a cube into 8 equal cubes with 0.5-cm edges. The small cubes have faces with an area of 0.25 cm^2. There are $6 \times 8 = 48$ such faces in all. Their total area is equal to 12 cm^2. The surface area has been doubled.

Thus, every splitting of a body increases its surface. Let us now break up a cube with a 1-cm side into small chips one micrometre long: 1 μm = 10^{-4} cm, so the large cube will be divided into 10^{12} pieces. Each piece (let us assume for the sake of simplicity that it, too, is cubic) has a surface area of 6 μm^2, i.e. 6×10^{-8} cm^2. The total surface area of the chips is equal to 6×10^4 cm^2, i.e. 6 m^2. And such a splitting is by no means the limit.

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*Adsorption should not be confused with absorption, which simply means taking in.

It is quite understandable that the specific surface area (i.e. the surface area of one gram of a substance) can be immense. It grows rapidly with the crushing of a substance—for the surface area of a grain decreases in proportion to the square of its linear dimension, and the number of grains in a unit of volume increases in proportion to the cube of this dimension. A gram of water poured onto the bottom of a glass has a surface area of several square centimetres. The same gram of water in the form of raindrops has a surface area of about tens of square centimetres. But one gram of droplets of fog has a surface area of several hundred square metres.

If you break up a piece of coal (the finer the better), it will be capable of adsorbing ammonia, carbon dioxide and many toxic gases. This last property has assured for coal an application in gas-masks. Coal breaks up particularly well, and the linear dimensions of its particles can be reduced to ten angstroms. Therefore, one gram of special coal has a surface area of several hundred square metres. A gas-mask with coal is capable of absorbing tens of litres of gas.

Adsorption is widely employed in the chemical industry. Molecules of different gases adsorbed on a surface come in close contact with each other and participate in chemical reactions more easily. In order to speed up chemical processes, one frequently makes use of finely split-up metals (nickel, copper and others) as well as of coal. Substances increasing the rate of a chemical reaction are called catalysts.

Osmosis

Among the living tissues, there are peculiar membranes which have the ability of letting water molecules pass through them, remaining impermeable to molecules of substances dissolved in water. The properties of these membranes are the causes of physical phenomena bearing the name "osmotic" (or simply "osmosis").

Imagine that such a semipermeable partition divides a pipe made in the form of the letter U into two parts. A solution is poured into one of the elbows of the pipe, and water or some other solvent into the other elbow. Having poured the same amount of liquid into both elbows, we shall discover with surprise that there is no equilibrium when the levels are equal. After a short time, the liquids settle down at different levels. Moreover, the level is raised in the elbow containing the solution. The water separated from the solution by the semipermeable partition tends to dilute the solution. It is just this phenomenon that bears the name *osmosis*, and the difference in height is called the *osmotic pressure*.

But what is the cause giving rise to osmotic pressure? In the right-hand elbow of the vessel (Figure 5.2), pressure is exerted only by water. In the left-hand elbow, the total pressure is the sum of the pressure of the water and that of the solute. But the door is open only for the water, and equilibrium in the presence of the semipermeable partition is established not when the pressure from the left equals the total pressure from the right, but when the pressure of the pure water is equal to the "water" portion of the pressure of the solution. The arising difference between the total pressures is equal to the pressure of the solute.

This excess of pressure is precisely the osmotic pressure. As experiments and computations show, the osmotic pressure is equal to the pressure exerted by a gas composed of the solute and occupying the same volume. It is therefore not surprising that osmotic pressure is measured in impressive numbers. The osmotic pressure arising in one litre of water when it dissolves 20 grams of sugar

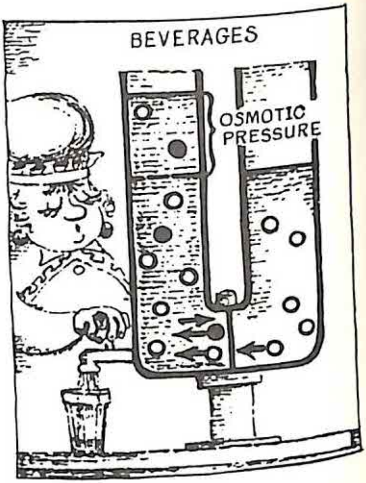


Figure 5.2

would balance a column of water 14 m in height.

Running the risk of arousing unpleasant memories in the reader, we shall now examine how the laxative action of certain salt solutions is related to osmotic pressure. The walls of the intestines are semipermeable to a number of solutions. If a salt does not pass through the walls of the intestines (this is true of Glauber's salt), then in the intestines there arises an osmotic pressure and this pressure "sucks" water through the tissues from the organism into the intestines.

Why does very salty water fail to quench one's thirst? It turns out that osmotic pressure is guilty of this, too. The kidneys cannot eliminate urine with the osmotic pressure greater than the pressure in the tissues of the organism. Consequently, an organism which has acquired salty sea water does not only fail to give it to the tissue liquids, but, on the contrary, eliminates water taken away from the tissues along with urine.

6. Molecular Mechanics

Frictional Forces

This isn't the first time that we are speaking of friction. And as a matter of fact, in telling about motion, how could we have managed without mentioning friction? Almost any motion of the bodies surrounding us is accompanied by friction. A car whose driver cut the motor comes to a halt; a pendulum comes to rest after many oscillations; a small metal ball thrown into a jar of sunflower oil slowly sinks. What makes bodies moving along a surface come to a halt? What is the cause of the slow falling of a ball in oil? We answer: the frictional forces arising during the motion of some bodies along the surfaces of others.

But frictional forces arise not only during motion.

You probably had to move furniture in a room. You know how hard it is to begin moving a heavy bookcase. The force counteracting this effort is called *static friction*.

Frictional forces also arise when we slide and roll objects. These are two somewhat different physical phenomena. We therefore distinguish between *sliding friction* and *rolling friction*. Rolling friction is tens of times less than sliding friction.

Of course, in certain cases sliding also proceeds with great ease. A sled slides easily along snow, and the sliding of skates along ice is even easier.

But what causes do frictional forces depend on? A frictional force between solid bodies depends little on the speed of the motion and is proportional to the weight of a body. If the weight of a body doubles, it will be twice as hard to set it in motion and to keep pulling it. We haven't expressed ourselves with complete precision: what is important is not so much the weight as the force that presses the body to the surface. If a body is light, but we press down hard on it with our hand, this will of course affect the force of friction. If we denote the force that presses a body to a surface (this is its weight in most cases) by P, the following simple formula will be valid for the frictional force F_{fr}:

$$F_{\text{fr}} = kP$$

But how are the properties of surfaces taken into account? For it is well known that one and the same sled will slide completely differently on the very same runners, depending on whether or not the runners are bound with iron. These properties are taken into account by the proportionality factor k, which is called the *friction coefficient*.

The friction coefficient of metal on wood is approximately equal to one-half. Only with a force of 1 kgf will one succeed in setting in motion a metallic slab with a mass of 2 kg which is lying on a smooth wooden table. But the friction coefficient of steel on ice is equal to only 0.027. That same slab can be moved on ice with a force of only 0.054 kgf.

One of the earliest attempts to lower the coefficient of sliding friction is depicted in a fragment of a mural from an Egyptian tomb dated approximately 1650 B.C. (Figure 6.1). We see a slave pouring oil under the runners of a sledge carrying a heavy statue.

The surface area does not occur in the above formula: the force of friction does not depend on the area of the contact surface between the bodies rubbing against each other. The same force is needed in order to set in motion, or to keep moving with a constant velocity, a wide sheet

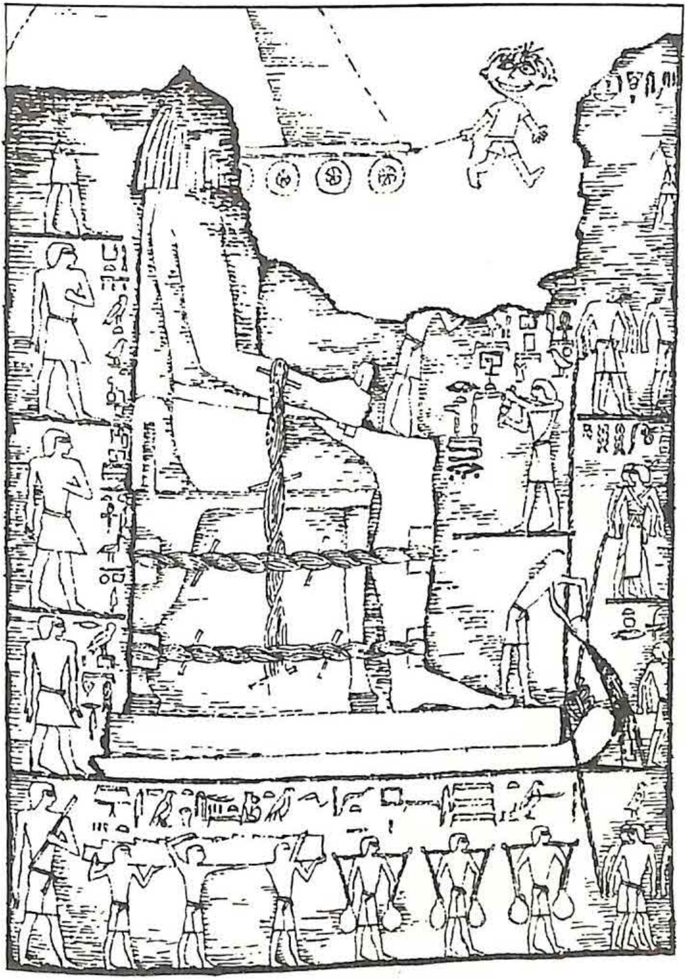


Figure 6.1

of steel weighing a kilogram and a kilogram weight which is supported by the surface of a small area.

And one more remark about forces of sliding friction. It is somewhat more difficult to set a body in motion than to keep it moving: the force of friction overcome at the first instant of motion (static friction) exceeds the subsequent values by 20-30%.

What can be said about the force of rolling friction, say, for a wheel? Just as for sliding friction, the greater the force that passes a wheel to a surface, the greater the rolling friction. Furthermore, the force of rolling friction is inversely proportional to the radius of the wheel. This is understandable: the larger the wheel, the less perceptible will be the roughness of the surface along which it is rolling.

If we compare the forces which must be overcome in making a body slide and roll, the difference we obtain is very impressive. For example, in order to pull a steel bar weighing 1 tonf along an asphalt pavement, a force of 200 kgf must be applied—only an athlete is capable of doing this. But even a child can roll this very same bar on a cart—a force not greater than 10 kgf is needed for this.

It's no wonder that rolling friction has "defeated" sliding friction. It was not without reason that humanity switched to wheel transport a very long time ago.

The replacement of runners by wheels is not yet a complete victory over sliding friction, for a wheel must be attached to an axle. At first glance it seems impossible to avoid the friction of the axle on the bearings. So people thought during the course of centuries and tried to decrease the sliding friction in bearings only by means of various lubricants. The services rendered by lubricants have not been small—sliding friction has been reduced by a factor of 8-10. But in a great many cases, the sliding friction, even with lubrication, is so considerable that

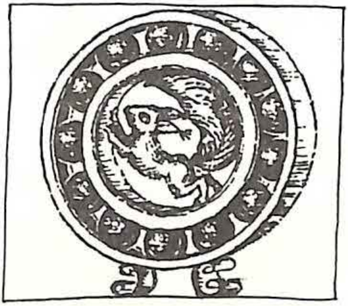


Figure 6.2

it costs too much. This circumstance greatly impeded the development of technology at the end of the past century. It was then that the remarkable idea arose of replacing the sliding friction in bearings by rolling friction. Ball bearings have accomplished this replacement. Small balls were fitted in between the axle and the bush. As the wheel turns, the balls roll along the bush, and the axle rolls on the balls. The construction of this mechanism is shown in Figure 6.2. Sliding friction was replaced by rolling friction in this manner, thus reducing frictional forces tens of times over.

The role played by ball and roller bearings in modern technology can scarcely be exaggerated. They are made with balls, with cylindrical rollers, with conical rollers. All machines, large and small, are equipped with such bearings. There exist ball bearings a millimetre in diameter; some bearings for large machines weigh over a ton. Balls for bearings (you have seen them, of course, in certain store windows) are manufactured with the most varying diameters—from fractions of a millimetre to several centimetres.

Viscous Friction in Liquids and Gases

Until now we have been speaking of "dry" friction, i.e. of the friction arising from the contact of two solid objects. But floating and flying bodies are also subject to the action of frictional forces. The source of friction has changed—dry friction is replaced by "wet" friction.

The resistance experienced by a body moving in water or air is subject to other laws, essentially different from the laws of dry friction, which we have spoken of above.

The rules for the behaviour of a liquid and a gas with respect to friction cannot be distinguished. Therefore, everything said below pertains to liquids and gases to the same degree. When we speak of a fluid, we will mean a liquid or a gas.

One of the distinctions between "wet" and dry friction consists in the absence of "wet static friction": an object suspended in water or air can, generally speaking, be started by an arbitrarily small force. But as for the frictional force experienced by a moving body, it will depend on the speed of the motion, on the form and dimensions of the body and on the properties of the fluid. The study of the motion of bodies in fluids has shown that there is no single law for "wet" friction, but there are two different laws: one is valid for motions with low speeds, and the other for motions with high speeds. The existence of two laws implies that the flow of a medium around a body moving in it takes place differently for motions of solids with high and low speeds.

For motions with low speeds, the force of resistance, or drag, is directly proportional to the speed and the linear dimensions of a body:

$$F \propto vL$$

How should we understand the proportionality to dimension if we aren't told what shape the body has?

What is meant is that for two bodies completely similar in shape (i.e. all of whose corresponding dimensions are in the same ratio), the ratio of the drag is the same as that of the linear dimensions of the bodies.

Drag depends to an enormous degree on the properties of a fluid. Comparing the frictional forces experienced by the same objects moving with identical speeds in various media, we see that the thicker or, as we say, the more viscous the medium, the greater the drag experienced by a body. It is therefore appropriate to call the friction under discussion *viscous friction*. It is quite understandable that air creates a negligible viscous friction, approximately 60 times less than water. A liquid can be "thin", like water, or very viscous, like sour cream and honey.

We can judge the degree of viscosity of a liquid either by the speed with which solid bodies fall in it or by the speed with which it pours through an opening.

It will take water several seconds to pour out of a half-litre funnel. A very viscous liquid will trickle out of it in hours, or even days. It is possible to give examples of even more viscous liquids. Geologists have called attention to the fact that in the craters of certain volcanoes spherical pieces are found in accumulations of lava on the inner sides. At first sight, it was completely impossible to understand how such a sphere might be formed out of lava inside a crater. This would be incomprehensible if lava were regarded as a solid. But if lava behaves like a liquid, it will drop down the crater just like any other liquid. But only a drop will be formed not in a fraction of a second but in the course of decades. When the drop becomes too heavy, it will break away and fall at the bottom of the crater.

It is clear from this example that real solid bodies and amorphous bodies, which, as we know, resemble liquids much more than crystals, should not be put on the same level. Lava is precisely such an amorphous body. It seems to be solid, but is actually a very viscous liquid.

What do you think, is sealing wax a solid? Take two corks and place them at the bottom of two cups. Pour any melted salt (for example, saltpeter—it is easily obtained) into one, and pour sealing wax into the other cup with a cork. Both liquids will harden and bury the corks. Put these cups away in the cupboard and forget about them for a long time. After several months, you will see the difference between sealing wax and salt. The cork drowned in salt will be at rest, as before, at the bottom of its cup. But the cork drowned in sealing wax will turn out to be on the top. But how did this occur? Very simply: the cork came to the surface in quite the same way as it would do in water. The only difference being is that of time: when the force of viscous friction is small, a cork comes to the surface instantly, but in very viscous liquids floating up takes months.

Forces of Resistance at High Speeds

But let us return to the laws of "wet" friction. As we explained, at low speeds the drag depends on the viscosity of a liquid, the speed of the motion and the linear dimensions of a body. Let us now consider the laws of friction for high speeds. But first of all, we must say what speeds are to be regarded as low, and what speeds as high. We are interested not in the numerical value of the speed but in whether the speed is sufficiently low for the law of viscous friction considered above to hold.

It turns out that it is impossible to name a number of metres per second such that the laws of viscous friction be applicable in all cases with lower speeds. The bounds of applicability of the law we have studied depends on the dimensions of a body and on the degree of viscosity and density of a liquid.

For air, "low" is a speed less than

$$\frac{0.75}{L}\,\text{cm/s}$$

for water, less than

$$\frac{0.05}{L}\,\text{cm/s}$$

and for viscous liquids like thick honey, less than

$$\frac{100}{L}\,\text{cm/s}$$

Consequently, the laws of viscous friction are scarcely applicable to air and especially to water: even for low speeds, of the order of 1 cm/s, they will apply only for tiny bodies with millimetre dimensions. The resistance experienced by a person diving into water is to no extent subject to the law of viscous friction.

But how can we explain the fact that the law governing the resistance of a medium changes with a change in speed? The causes must be sought in the change in the character of the flow of a liquid around a body moving in it. Two circular cylinders moving in a liquid are depicted in Figure 6.3 (their axes are perpendicular to the drawing). For a slow motion, the liquid flows smoothly around the moving object—the drag which it has to overcome is the force of viscous friction (Figure 6.3*a*). For a high speed, behind the moving body there arises a complicated irregular motion of the liquid (Figure 6.3*b*). Various streams appear and disappear, forming fantastic figures, rings and eddies. The picture made by the streams is changing all the time. The appearance of this motion, called turbulent, radically changes the law of resistance.

Turbulent resistance depends on the speed and dimensions of an object in an entirely different way than viscous resistance: it is proportional to the square of the

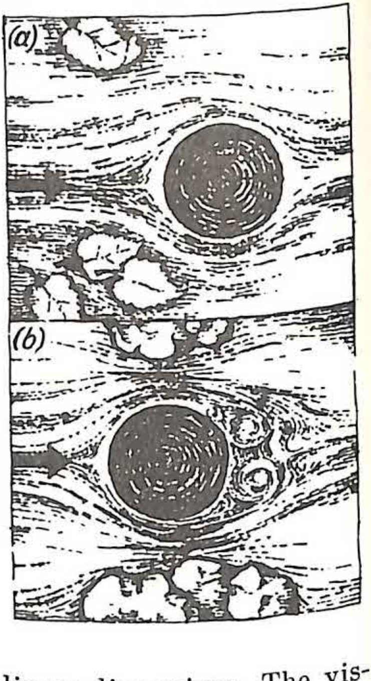


Figure 6.3

speed and the square of the linear dimensions. The viscosity of a liquid during this motion ceases to play an essential role; the determining property becomes its density, with the drag proportional to the first power of the density of the fluid. Therefore, the following formula holds for the force F of turbulent resistance:

$$F \propto \rho v^2 L^2$$

where v is the speed of the motion, L are linear dimensions of the object, and ρ is the density of the medium. The numerical proportionality factor, which we haven't written down, has various values depending on the shape of the body.

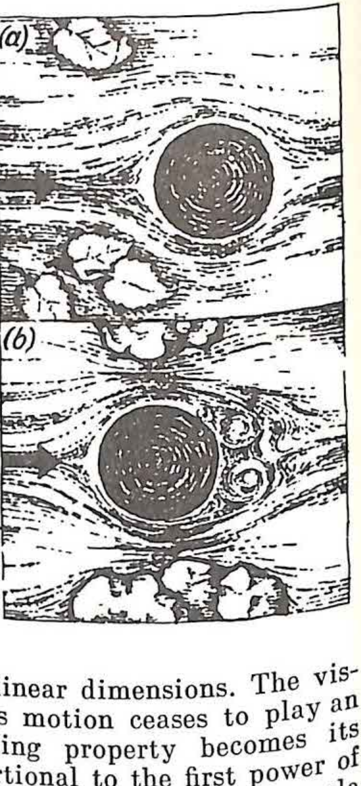
Streamline Shape

Motion in the air, as has been said above, is almost always "speedy", i.e. the basic role is played by turbulent and not viscous resistance. Airplanes, birds and parachutists experience turbulent resistance. If a person falls through the air without a parachute, then after a certain time he begins falling uniformly (the force of resistance balances the weight), but with quite a considerable speed, of the order of 50 m/s. The opening of a parachute leads to a sharp deceleration of the fall—the same weight is now balanced by the resistance of the canopy. Since the force of resistance is proportional to the speed of the motion as well as to the linear dimensions of the falling object, the speed will decrease as many times as the linear dimensions of the falling body increase. The diameter of a parachute is about 7 m, whereas the "diameter" of a man's body is about one metre. The speed of the fall will be decreased to 7 m/s. One can land safely with such a speed.

We must say that the problem of increasing the resistance is far more easily solved than the converse problem. Reducing the air resistance on a car or an airplane, or the water resistance on a submarine, is one of the most important and difficult technological problems.

It proves possible to decrease turbulent resistance by a large factor by changing the shape of a body. For this one must reduce to a minimum the turbulent motion, which is the source of the resistance. This is achieved by, as they say, streamlining the object.

But what shape is best in this sense? It would appear at first sight that the body should be shaped so that the forward side comes to a point. Such a point, it seems, should "cleave" the air most successfully. But it proves important not to cleave the air but to disturb it as little as possible so that it flows smoothly around the object.



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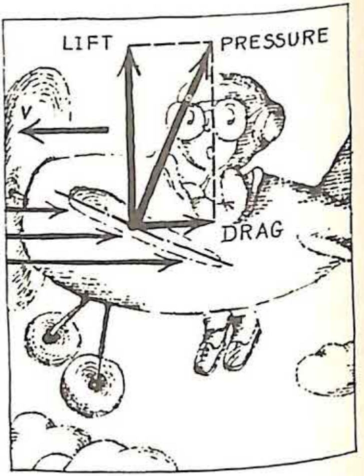

Figure 6.4

The best profile for a body moving in a fluid is the one whose shape is obtuse in front and pointed behind*. With such a shape, the fluid would flow smoothly off the point and turbulence would be reduced to a minimum. Sharp edges should not in any case be put in front, since there they would create turbulence.

The streamline shape of an airplane wing creates not only the least resistance to the motion but also the greatest lift, when the fairing is inclined upwards from the direction of the motion. Flowing around a wing, the air pushes against it mainly in the direction perpendicular to its plane (Figure 6.4). It is clear that for an inclined wing this force is directed upwards.

The lift grows with an increase in the angle of attack. But reasoning based solely on geometrical considerations would lead us to the false conclusion that the greater the

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*The pointed prows of boats and sea-going vessels are needed for "breaking" waves, i.e. only when the motion is taking place along the surface.

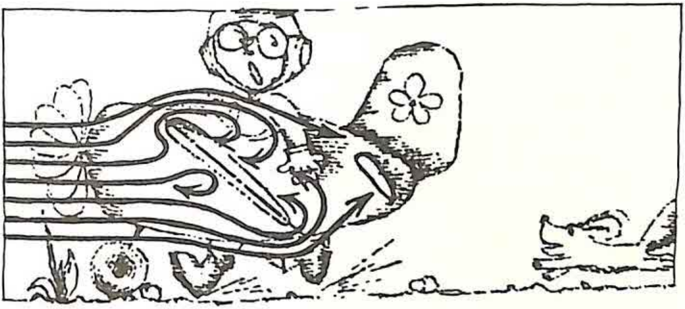

Figure 6.5

angle of attack, the better. But as a matter of fact, as the angle of attack is increased, the smooth flow of the plane becomes more and more difficult, and at a certain value for this angle, as illustrated in Figure 6.5, violent turbulence arises; the drag sharply increases and the lift decreases.

Disappearance of Viscosity

Very often, in explaining some phenomenon or describing the behaviour of one or another group of bodies, we refer to well-known examples. It is quite obvious that this object should be moving in such a manner, we say, for other bodies also move according to the very same rules. The explanation reducing the new to that which we have already come across in the course of our lives always satisfies the majority. We therefore did not have any particular difficulty in explaining to the reader the laws in accordance with which liquids move—for everyone has seen how water flows, and the laws governing this motion seem quite natural.

However, there is one perfectly amazing liquid which does not resemble any other liquid and moves in accordance with special laws characteristic of it alone. It is liquid helium.

We have already said that liquid helium remains in the liquid phase right down to the temperature of absolute zero. However, helium above 2 K (more precisely, 2.19 K) and helium below this temperature are two completely different liquids. Above two degrees, the properties of helium in no way distinguish it from other liquids. Below this temperature, helium becomes a miraculous liquid. This miraculous helium is called helium II.

The most striking property of helium II is its *superfluidity*, i.e. complete lack of viscosity, discovered by P. L. Kapitza in 1938.

In order to observe superfluidity, a vessel is made with a very fine slit at the bottom—of only half a micrometre in width. An ordinary liquid hardly seeps through such a slit; helium also behaves this way at temperatures above 2.19 K. But as soon as the temperature becomes barely less than 2.19 K, the speed with which helium flows out of such a vessel grows by leaps and bounds—by a factor of at least several thousand. Helium II almost momentarily flows through the narrowest clearance, i.e. it completely loses its viscosity. The superfluidity of helium leads to an even stranger phenomenon. Helium II is capable of "climbing out" of the glass or test tube into which it was poured. A test tube with helium II is placed in a Dewar vessel over a helium bath. "Without rhyme or reason", helium rises along the wall of the test tube in the form of a very fine, completely unnoticeable film and overflows; drops fall from the bottom of the test tube.

It should be recalled that thanks to capillary forces, which were discussed on p. 45, the molecules of every liquid wetting the wall of a vessel climb up this wall and form the finest film on it whose width is of the order of

10^{-6} cm. This film cannot be seen by an eye, and in general does not manifest itself in any way for an ordinary viscous liquid.

The picture changes completely if we are dealing with helium devoid of viscosity. In fact, a narrow slit does not hinder the movement of superfluid helium, and a thin film on a surface is just the same as a narrow slit. A liquid without viscosity flows in a very fine layer. The film covering the surface forms a siphon over the edge of the glass or test tube through which the helium overflows the vessel.

It is obvious that we do not observe anything of the kind in the behaviour of an ordinary liquid. A liquid of standard viscosity is practically unable to "make its way" through a siphon of negligible thickness. Such a motion is so slow that the outflow would last millions of years.

Thus, helium II is devoid of any viscosity. The conclusion that a solid should move without friction in such a liquid would appear to follow from this with iron logic. Let us take a disc on a string, place it in liquid helium II and twist the string. Leaving this uncomplicated device alone, we create something like a pendulum—the string with the disc will oscillate and periodically twist first in one and then in another direction. If there were no friction, we should expect the disc to oscillate perpetually. But nothing of the kind! After a comparatively short time, approximately the same as for ordinary helium I (i.e. helium at a temperature above 2.19 K), the disc comes to a halt. But how will this happen? When flowing through a slit, helium behaves like a liquid without viscosity, but behaves like an ordinary viscous liquid in relation to bodies moving in it. It is this, to be sure, that is in fact completely extraordinary and incomprehensible.

It now remains for us to recall that helium does not solidify right up to absolute zero. The crux of the problem is that the ideas about motion which we are accustomed to are not suitable any more. If helium has remained liquid "illegally", should we be surprised by the lawless behaviour of this liquid?

It is only possible to understand the behaviour of liquid helium from the point of view of the new conceptions of motion, quantum mechanics. Let us try to give a general idea of how quantum mechanics explains the behaviour of liquid helium.

Quantum mechanics is an extremely intricate theory, which is very hard to understand, and so the reader should not be surprised that the explanation looks even stranger than the phenomena themselves. It turns out that every particle of liquid helium participates simultaneously in two motions: one motion is superfluid, unrelated to viscosity, and the other is ordinary.

Helium II behaves as if it consisted of a mixture of two liquids moving completely independently, "one through the other". One liquid behaves normally, i.e. possesses an ordinary viscosity, while the other component part is superfluid.

When helium flows through a slit or overflows a glass, we observe the effect of superfluidity. But during the oscillation of a disc submerged in helium, friction is created because it is inevitable in the normal part of helium.

The ability to participate in two distinct motions also gives rise to completely unusual heat-conducting properties of helium. As has been already said, liquids in general conduct heat rather poorly. Helium I also behaves like an ordinary liquid. But when the transformation into helium II takes place, its thermal conductivity grows about a thousand million-fold. Therefore, helium II conducts heat better than the best ordinary heat conductors, such as copper and silver.

The fact is that the superfluid motion of helium does not participate in the heat transfer. Consequently, when there is a difference in temperature within helium II, there arise two currents in opposite directions, and one of them—the normal one—carries heat with it. This does not at all resemble ordinary thermal conductivity. In an ordinary liquid, heat is transferred by means of molecular collisions. In helium II, heat flows together with the ordinary part of helium—flows like a liquid. Here at last the term "heat flow" is fully justified. It is precisely such a method of transferring heat that leads to an immense thermal conductivity.

This explanation of the thermal conductivity of helium may seem so strange that you will refuse to believe it. But it is possible to convince oneself first-hand of the validity of what has been said by means of the following conceptually simple experiment.

In a tub with liquid helium there is a Dewar vessel filled to the brim with helium. The vessel is connected to the tub by means of a capillary branch piece. The helium inside the vessel is heated by an electric spiral, but heat does not pass to the surrounding helium through the walls of the vessel, since they do not transmit heat. Near the end of the capillary tube there is a vane suspended on a fine thread. If the heat is flowing like a liquid, it should turn the vane. This is precisely what happens. Moreover, the amount of helium in the vessel does not change. How can this miraculous phenomenon be explained? In only one way: during heating there arises a current of the normal part of the liquid from the heated place to the cold, and a current of the superfluid part in the opposite direction. The amount of helium at each point does not change, but since the normal part of the liquid moves together with the heat transfer, the vane turns as a result of the viscous friction of this part and remains deflected as long as heating continues.

Another conclusion also follows from the fact that superfluid motion does not transfer heat. We have spoken above about the "creeping" of helium over the brim of a glass. But the superfluid part "climbs out" of the glass, while the normal part remains there. Heat is connected to only the normal part of helium and does not accompany the superfluid part which is climbing out of the glass. Hence, as helium climbs out of the vessel, one and the same amount of heat will be shared by a smaller and smaller amount of helium—the helium remaining in the vessel should warm up. This is actually observed during experiments.

The masses of the helium partaking in superfluid and normal motion are not identical. Their ratio depends on the temperature. The lower the temperature, the greater the superfluid part. All of the helium becomes superfluid at absolute zero. As the temperature rises, a larger and larger part of the helium begins to behave normally, and at the temperature of 2.19 K, all of the helium becomes normal, acquiring the properties of an ordinary liquid.

But the reader already has some questions in his mind: What precisely is called superfluid helium, how can a particle of liquid participate simultaneously in two motions and how can the very fact of two motions of a single particle be explained?... Unfortunately, we are obliged to leave all these questions unanswered. The theory of helium II is too complicated, and it is necessary to know a great deal in order to understand it.

Plasticity

Elasticity is the ability of a body to recover its form after a force ceased acting on it. If a kilogram weight is hung on a 1-m steel wire with a cross-sectional area of 1 mm^2, the wire will be stretched. The stretching is negligible, only 0.5 mm in all, but it is not difficult to observe. If the load is removed, the wire will contract by the same 0.5 mm, and so its length will return to its former value. Such a deformation is called *elastic*.

Let us note that a wire of 1-mm^2 cross-section under the action of a force of 1 kgf and a wire of 1-cm^2 cross-section under the action of a force of 100 kgf are, as one says, under the same conditions of mechanical stress. Therefore, the behaviour of a material must always be described by indicating not the force (which would be pointless if the cross-section of a body is unknown), but the stress, i.e. the force per unit of area. Ordinary bodies—metals, glass, stones—can be stretched elastically by only several per cent at best. Rubber possesses outstanding elastic properties. Rubber can be stretched elastically by several hundred per cent (i.e. made two or three times longer than it was originally), and when we let such a rubber band go, we see that it returns to its initial state.

All bodies without exception behave elastically under the action of small forces. However, a limit of elasticity appears earlier for some bodies and considerably later for others. For example, the elastic limit for such soft metals as lead has already been reached when a load of 0.2-0.3 kgf is hung on a wire of 1-mm^2 cross-section. This limit is approximately 100 times as great, i.e. about 25 kgf, for such hard materials as steel.

With respect to large forces exceeding the elastic limit the various bodies can be roughly divided into two classes: those like glass, i.e. fragile, and those like clay, i.e. plastic.

If you press a piece of clay with your finger, it will leave its imprint, containing even the intricate whirls drawn on its skin. If you strike a piece of soft iron or lead with a hammer, a clear trace will be left. There is no longer any force, but the deformation remains—it is called *plastic* or *permanent*. You will not succeed in obtaining such residual effects with glass: if you persist in this endeavour, the glass will break. Certain metals and alloys, such as cast iron, are just as fragile. An iron pail will flatten, but a cast iron pot will crack, under the blows of a hammer. One can judge the strength of fragile bodies by the following figures. In order to convert a piece of cast iron into powder, one must act with a force of about 50-80 kgf per square millimetre of surface area. This figure falls to 1.5-3 kgf for a brick.

As for every classification, the division of bodies into fragile and plastic is, to a fair degree, relative. First of all, a body which is fragile at a low temperature can become plastic at higher temperatures. Glass can be superbly processed as a plastic material if it is heated to a temperature of several hundred degrees. Soft metals, such as lead, can be forged cold, but hard metals yield to forging only when burning hot. A rise in temperature sharply increases the plasticity of a material.

One of the essential features of metals, which has made them irreplaceable building materials, is their hardness at room temperatures and plasticity at high temperatures: an incandescent metal can be easily given the required form, but it is only possible to change this form at room temperature by means of very substantial forces.

The internal structure of a material influences its mechanical properties in an essential way. It is obvious that cracks and holes weaken the apparent strength of a body and make it more fragile.

The ability of plastically deformable bodies to strengthen is remarkable. A single crystal of a metal is very soft when it has just grown up out of a melt. Crystals of many metals are so soft that they are easily bent with one's fingers; however, one will not succeed in straightening them out. Strengthening has taken place. This same specimen can now be plastically deformed only by means of a considerably greater force. It turns out that plasticity is not only a property of a material, but also a property of its treatment.

Why are instruments made not by casting metals, but by forging them? The reason is obvious—a metal subjected to forging (or rolling, or drawing) is much stronger than cast metal. No matter how much we forge a metal, we cannot increase its strength beyond a certain limit, which is called the yield stress. For steel it is between 30 and 50 kgf/mm^2. This figure has the following meaning. If a one-pood weight (below the yield stress) is hung on a wire of 1-mm^2 cross-section, the wire will begin stretching and strengthening simultaneously. The stretching will therefore quickly cease—the weight will hang calmly on the wire. But if a two- or three-pood weight (above the yield stress) is hung on such a wire, the picture will be different. The wire will keep stretching until it breaks. Let us emphasize once again that the mechanical behaviour of a body is determined not by the force, but by the stress. A wire of a cross-section of 100 μm^2 will yield under the action of a load of (30-50) $\times$ 10^{-4} kgf, i.e. 3-5 gf.

Dislocations

Proving that plastic deformation is a phenomenon of immense significance in engineering practice would be forcing an open door. Smith and die forging, rolling sheets, drawing wire are all techniques based on the plastic working of metals leading to their deformation.

We could understand nothing about plastic deformation if we considered the crystallites of which a metal consists to be ideal fragments of space lattices.

The theory of the mechanical properties of an ideal crystal was worked out long ago, at the beginning of the century. This theory disagrees with experimental data about a thousand-fold. If all crystals were ideal, their tensile strength would be many orders of magnitude higher than that actually observed. Then plastic deformation would require huge forces.

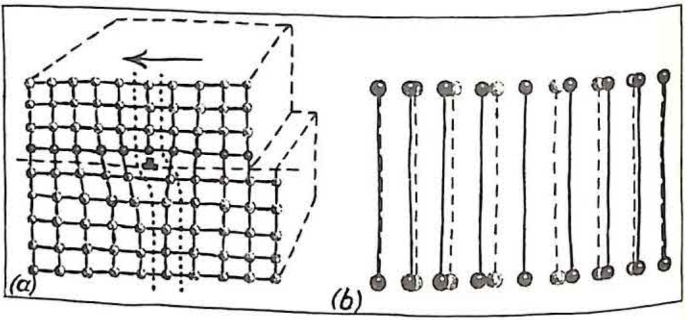

Figure 6.6

Hypotheses had been suggested much earlier than sufficient facts accumulated to support them. It was obvious to investigators that the only way to reconcile theory with practice was to assume that crystallites have certain defects. Various conjectures could be made, of course, on the nature of these defects. But the picture began to clear up only after the most sophisticated equipment for investigating the structure of matter had been made available to physicists. It was found that an ideal portion of a lattice (called a block) has dimensions of the order of several millionths of a centimetre. These blocks are disoriented with respect to one another by angles within a second or a minute of arc.

Many facts accumulated by the end of the twenties led to the important contention that the chief (though not only) defect of a real crystal is a regular displacement that was named a *dislocation*. A simple, or linear, dislocation is illustrated by the model in Figure 6.6. The essence of the defect, as is evident, is that there are places in the crystal that seem to contain an "extra" atomic plane (from which its name "extraplane" is derived). The horizontal dash line in Figure 6.6*a* divides two blocks. The

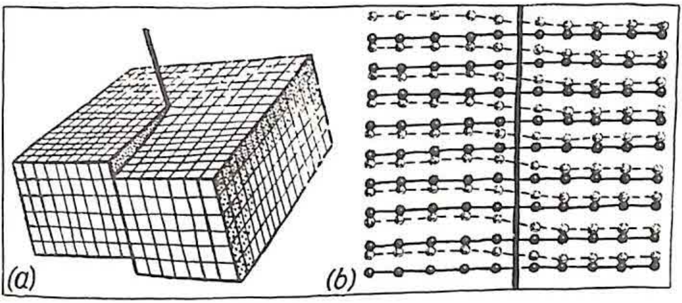

Figure 6.7

upper part of the crystal is in compression, and the lower part in tension. The effect of the dislocation on the crystal is rapidly dissipated as seen in Figure 6.6*b* which is a sort of "top" view of the left-hand drawing

Another type of dislocation, frequently found in crystals, is the screw dislocation. It is illustrated schematically in Figure 6.7. Here the lattice is divided into two blocks, one of which has slipped, as it seems, by one lattice constant with respect to the other. Maximum distortion is concentrated at the vertical axis shown in the diagrams. The region adjoining this axis is what is called a screw dislocation.

We shall understand the nature of this distortion better if we look at the other diagram (Figure 6.7*b*), which illustrates two adjacent atomic planes on the two sides of the vertical plane passing through the axis (the one along which slip has occurred). With respect to the three-dimensional view, this is a projection showing the plane from the right. Here we see the axis of the screw dislocation, the same as in the other drawing. The atomic plane belonging to the right-hand block is shown by full lines; that belonging to the left-hand block by dash lines. The black circles are closer to the reader than the light ones. It is evident from the drawing that a screw dislocation is another type of distortion differing from that of a linear distortion. There is no extra row of atoms The essence of the distortion is that the rows of atoms change their nearest neighbours near the dislocation axis. They are bent downwards to align themselves with the neighbours located one storey below.

Why is this called a screw dislocation? Imagine that you are strolling along the atoms (after reducing your size to subatomic dimensions) and have decided to pass around the dislocation axis. It is obvious that if you start your journey on the lowest plane you will find yourself one storey higher after each turn. Finally, you will emerge on the top surface of the crystal, as if you had been climbing winding stairs in a helix like the thread of a screw. In our drawing, the climb is in the counterclockwise direction. If the slip of the blocks had been in the opposite direction, your journey would have been clockwise.

We are now ready to answer the question of how plastic deformation takes place.

Assume that we want to shift the upper half of a crystal with respect to the lower one by one interatomic distance. Evidently, we must roll all the atoms in the shear plane over one another. It is an entirely different matter when a shear force acts on a crystal containing a dislocation.

Figure 6.8 illustrates a close packing arrangement of spheres (only the end spheres of the rows of atoms are shown), containing a linear dislocation, consisting of a linear void (something like a fissure) between two of the upper rows. We begin to shift the upper block to the right with respect to the lower one. To help you understand what is happening, we have given numbers to the rows, with primed numbers for the spheres of the compressed (lower) layer. At some initial moment, the "fissure"

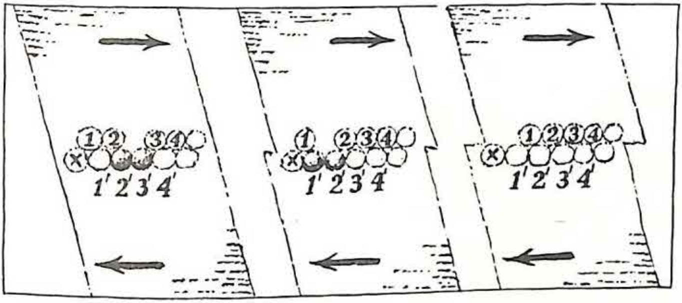

Figure 6.8

is between rows *2* and *3*; the compressed rows are *2′* and *3′*. As soon as the shifting force is exerted, row *2* moves into the "fissure"; now row *3′* can "breathe freely", but row *1′* will have to squeeze into less space. What happened? The whole dislocation moved to the left, and its motion continues in the same way until it (the dislocation) "emerges" from the crystal. The result is a shift over one row of atoms, i.e. the same as in the shear of a perfect crystal.

It is evidently unnecessary to prove that shear by dislocation motion requires much less force. In the shear of a perfect crystal we had to overcome the interaction between atoms in rolling over all the rows simultaneously. In dislocation shear, only a single row of atoms is involved at each instant.

Calculations indicate that the strength of crystals in shear, assuming there are no dislocations, should be a hundred times more than that actually observed in experiments. The presence of even a slight number of dislocations can reduce the strength of the material by a substantial factor.

The preceding discussion poses a question that must be cleared up. It is evident from the drawing (see Figure 6.8) that the applied force "drives" the dislocation out of the crystal. This implies that the crystal becomes stronger and stronger as we increase the degree of deformation. Finally, when the last dislocation is eliminated, the crystal should, according to the theory, become about a hundred times stronger than a perfect regular crystal. The crystal actually is strengthened in the course of deformation, but far from a hundred-fold. The screw dislocations save the day. It was established (and here the reader will just have to take our word for it because it is so difficult to illustrate with a drawing) that screw dislocations cannot be easily "driven" out of a crystal. Moreover, shear of the crystal may take place with the aid of dislocations of both types. Dislocation theory satisfactorily explains the features of shear phenomena along crystal planes. According to up-to-date views, plastic deformation of crystals consists in the motion of disorder along the crystal.

Hardness

Strength and hardness do not go hand in hand with each other. A rope, a scrap of cloth and a silk thread can possess a great deal of strength—a considerable stress is needed to tear them. Of course, nobody will say that rope and cloth are hard materials. And conversely, the strength of glass is not great, but glass is a hard material.

The concept of hardness used in technology is taken from everyday practice. *Hardness* is the resistance to penetration. A body is hard if it is difficult to scratch it, difficult to leave an imprint on it. These definitions may seem somewhat vague to the reader. We are accustomed to physical concepts being expressed in terms of numbers. But how can this be done in relation to hardness?

One rather primitive method, which is nevertheless useful in practice, has already been employed for a long time by mineralogists. Ten definite minerals are arranged in a series. The first is diamond, followed by corundum, then topaz, quartz, feldspar, apatite, fluor-spar, calcite, gypsum and talc. The series is sorted out in the following manner: diamond leaves its mark on all minerals, but none of these minerals can scratch diamond. This means that diamond is the hardest mineral. The hardness of diamond is evaluated by the number 10. Corundum, which follows diamond in the series, is harder than all the minerals below it—corundum can scratch them. Corundum is assigned the hardness number 9. The numbers 8,7 and 6 are assigned to topaz, quartz and feldspar, respectively, on the same grounds. Each of them is harder than (i.e. can scratch) all the minerals below it, and softer than (can itself be scratched by) the minerals having greater hardness numbers. The softest mineral, talc, has hardness number 1.

A "measurement" (this word must be taken in quotation marks) of hardness with the aid of this scale consists in finding the place for the mineral of interest to us in a series containing the ten chosen standards. If the unknown mineral can be scratched by quartz, but leaves its mark on feldspar, its hardness is equal to 6.5.

Metallurgists use a different method for determining hardness. A dent is made on the material being tested by pressing a steel ball 1 cm in diameter against it with a standard force (ordinarily 3000 kgf). The radius of the small pit so formed is taken as the hardness number.

Hardness with respect to scratching and hardness with respect to pressing do not necessarily correspond, and one material may prove to be harder than another when tested by scratching but softer when tested by pressing.

Consequently, there is no universal concept of hardness independent of the method of measurement. The concept of hardness is a technological and not a physical concept.

Sound Vibrations and Waves

We have already given the reader a lot of information about oscillations. How a pendulum and a ball on a spring oscillate and what regularities there are in the oscillation of a string, all of this was studied in one of the chapters of the first book. We haven't spoken about what takes place within the air or some other medium when a body located in it performs oscillations. There is no doubt that the medium cannot remain indifferent to vibrations. An oscillating object pushes the air, displacing the air particles from the positions in which they were previously located. It is also obvious that this cannot be limited to the influence on only the adjacent layer of air. The body will push the nearest layer, this layer presses against the next one, and so layer after layer, particle after particle, all of the surrounding air is brought into motion. We say that the air has come to a vibrating state, or that *sound vibrations* are taking place in the air.

We call the vibrations of the medium sound vibrations, but this does not mean that we hear all of them. Physics uses the concept of sound vibrations in a broader sense. The question as to which sound vibrations are heard will be discussed below.

We are dealing with air only because sound is most often transmitted through air. But there are, of course, no special properties of air which would give it a monopoly to perform sound vibrations. Sound vibrations arise in any medium capable of being compressed, but since there are no incompressible bodies in nature, the particles of any material can therefore find themselves in this state. The study of such vibrations is usually called *acoustics*.

Each particle of air remains at one place, on 'the average, during sound vibrations—it only performs oscillations about its equilibrium position. In the simplest case, a particle of air can perform a harmonic oscillation, which, as we recall, takes place in accordance with the sinusoidal law. Such an oscillation is characterized by the maximum displacement of a particle from its equilibrium position (amplitude) and the period of the oscillation, i.e. the time required to perform a complete oscillation.

The concept of the *frequency of vibration* is used more often than that of the period for describing the properties of sound vibrations. The frequency $\nu = 1/T$ is the reciprocal of the period. The unit of frequency is the inverse second (s^{-1}). If the frequency of vibration is equal to $100\ s^{-1}$, this means that during one second a particle of air performs 100 complete vibrations. Since in physics we must deal rather often with frequencies which are many times greater than a hertz, the units *kilohertz* and *megahertz* are widely applied; $1\ \text{kHz} = 10^3\ \text{Hz}$, $1\ \text{MHz} = 10^6\ \text{Hz}$.

The speed of a vibrating particle is maximum when it is passing through its equilibrium position. On the contrary, in positions of maximum displacement, the speed of a particle is, naturally, equal to zero. We have already said that if the displacement of a particle is subject to the law of harmonic oscillation, the change in its speed of vibration obeys the same law. If we denote the maximum value (amplitude) of the displacement by s_0, and of the speed by v_0, then $v_0 = 2\pi s_0/T$, or $v_0 = 2\pi\nu s_0$. Loud conversation brings air particles into vibration with an amplitude of only several millionths of a centimetre. The maximum value of the speed will be of the order of 0.02 cm/s.

Another important physical quantity varying together with the displacement and speed of a particle is the *excess pressure*, also called the *sound pressure*. A sound vibration of air consists in a periodic alternation of compression and rarefaction at each point in the medium. The air pressure at any place is now higher, now lower than the pressure which would be there in the absence of sound. This excess (or insufficiency) of pressure is just what is called the

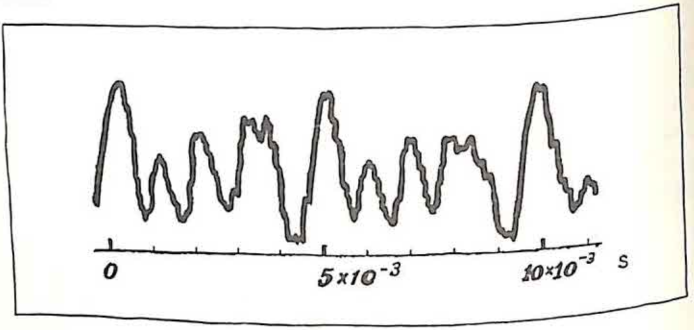

Figure 6.9

sound pressure. Sound pressure is a small fraction of standard atmospheric pressure. For a loud conversation the sound pressure amplitude will be equal to approximately one-millionth of the atmospheric pressure. Sound pressure is directly proportional to the speed of the vibration of a particle, where the ratio of these physical quantities depends only on the properties of the medium. For example, a speed of vibration of 0.025 cm/s corresponds to a sound pressure in air of 1 dyn/cm^2.

A string vibrating in accordance with a sinusoidal law brings air particles into harmonic oscillation. Noises and musical sounds lead to a considerably more complicated picture. A graph of sound vibrations, namely of the sound pressure as a function of time, is shown in Figure 6.9. This curve bears little resemblance to a sine wave. It turns out, however, that any arbitrarily complicated vibration can be represented as the result of superposing a large number of sine waves with different amplitudes and frequencies. These simple vibrations make up, as is said, the spectrum of the complex vibration. Such a superposition of vibrations is shown for a simple example in Figure 6.10.

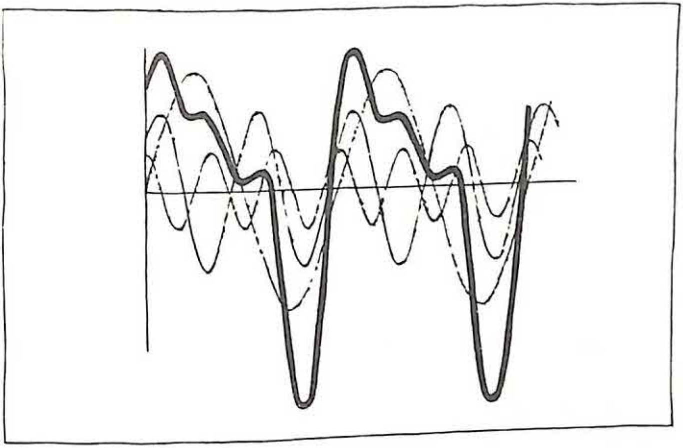

Figure 6.10

If sound were propagated instantaneously, all the air particles would vibrate in unison. But sound is not propagated instantaneously, and the masses of air lying on the lines of propagation are brought into motion in turn, as if caught up by a wave coming from some source. In exactly the same way, a chip lies calmly on the water until the circular waves from a pebble thrown into the water catch it up and make it vibrate.

Let us confine our attention to a single vibrating particle and compare its behaviour with the motion of other particles lying on the same line of sound propagation. An adjacent particle will start vibrating somewhat later, the next particle still later. The delay will keep increasing until we meet a particle which is lagging behind by a whole period and is therefore vibrating in time with the initial particle. So an unsuccessful runner, who has fallen behind the leader by an entire lap, can cross the finish

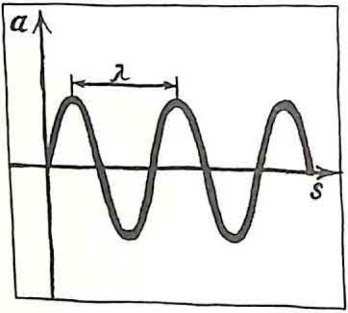

Figure 6.11

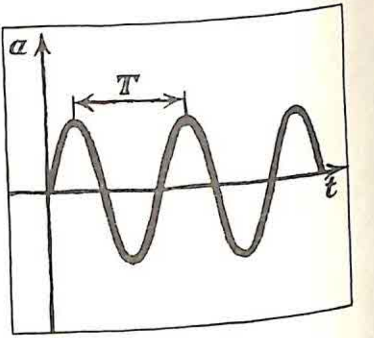

Figure 6.12

line simultaneously with the leader. But at what distance will we meet the point which is vibrating in time with the initial particle? It is not hard to see that this distance λ is equal to the product of the speed of propagation of sound c by the period of vibration T. The distance λ is called the *wavelength*:

$$\lambda = cT$$

We will find points vibrating in time after intervals of length λ. Points separated by a distance of $\lambda/2$ will move relative to each other like an object vibrating perpendicularly to a mirror moves with respect to its image.

If we depict the displacement (or speed, or sound pressure) of all the points lying on a line of propagation of a harmonic sound, then a sine wave is again obtained.

The graphs of the wave motion and the vibration should not be confused. There is a strong resemblance between Figures 6.11 and 6.12, but the distance is plotted along the horizontal axis in the former, while the time in the latter. One figure represents the development of the vibration in time, and the other an instantaneous "photograph" of the wave. It is evident from the comparison of these two graphs that the wavelength may also be called its spatial period: the quantity λ plays the same role in space as T plays in time.

In a graph of a sound wave, the displacements of a particle are plotted along the vertical axis, and the horizontal axis is the direction of the propagation of the wave along which the distance is marked off. This might suggest the false idea that the particles are displaced perpendicularly to the direction of the propagation of the wave. In reality, air particles always vibrate along the direction of the propagation of the sound. Such a wave is called *longitudinal*.

The speed of light is incomparably greater than that of sound; light is propagated practically instantaneously. Thunder and lightning occur at the same instant; we see a flash of lightning practically at the instant of discharge, but the sound of thunder reaches us at a speed of approximately one kilometre in three seconds (the speed of sound in air is 330 m/s). Hence, when we hear the thunder, there is no longer any danger in being struck by that particular bolt of lightning.

Knowing the speed of the propagation of sound, we can usually determine how far away a thunderstorm is raging. If 12 seconds have passed from the moment of the flash of lightning to that of the peal of thunder, the storm is therefore 4 kilometres away.

The speed of sound in gases is approximately equal to the average speed of the motion of their molecules. It is also independent of the density of a gas and proportional to the square root of its absolute temperature. Liquids propagate sound faster than gases. Sound is propagated in water with a speed of 1450 m/s, i.e. 4.5 times as fast as in air. The speed of sound in solids is even greater; for example, it is about 6000 m/s in iron.

When sound passes from one medium to another, the speed of its propagation changes. But another interesting phenomenon also occurs simultaneously—the partial reflection of sound from the boundary between the two media. The fraction of sound reflected depends mainly on the ratio of the densities. In the case when sound passing through air is incident upon a solid or liquid surface, or vice versa, from dense media into air, the sound is almost completely reflected. When sound passes from air to water or, conversely, from water to air, only one-thousandth of the sound passes into the latter medium. If both media are dense, the ratio between the transmitted and the reflected sound can be small. For example, 13% of the sound will pass from water into steel or from steel into water, and 87% will be reflected.

The reflection of sound is widely applied in navigation. The construction of an instrument for measuring depths, the sonic depth finder, is based on it. A source of sound is placed under water on one side of a ship (Figure 6.13). A discontinuous sound creates sound rays, which will make their way through the watery thickness to the bottom of the sea or river, be reflected from the bottom and return in part to the ship, where sensitive instruments will catch them. Accurate clocks will show how much time the sound needs for this journey. The speed of sound in water is known, and it is possible to obtain precise information about the depth by means of a simple calculation.

By aiming the sound forward or sideways instead of downwards, it is possible to determine with its aid whether or not there are dangerous reefs or deeply submerged icebergs near the ship.

All the particles of air surrounding a vibrating body are in a state of vibration. As we explained in the first book, a mass point vibrating in accordance with the sinusoidal law possesses a definite and constant total energy.

When a vibrating point passes through its equilibrium position, its speed is maximum. Since the displacement

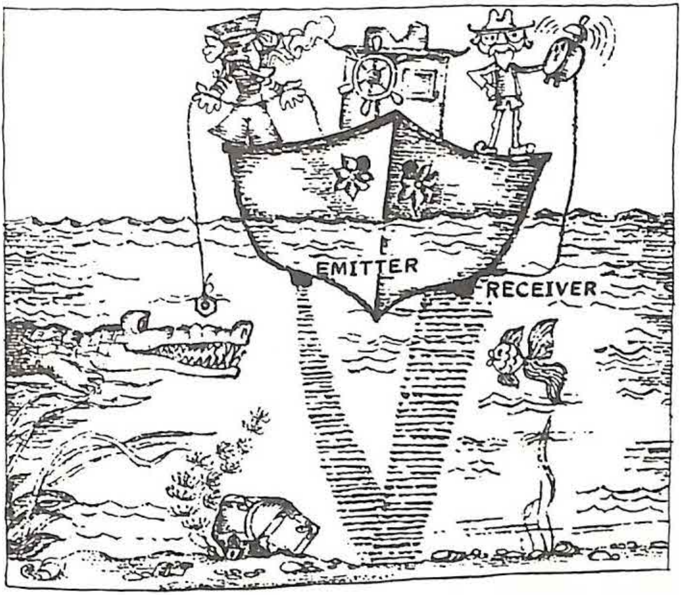

Figure 6.13

of the point is equal to zero at this instant, the entire energy is kinetic:

$$E = \frac{mv^2_{\max}}{2}$$

Consequently, the total energy is proportional to the square of the amplitude of the speed of vibration.

This is also true for particles of air vibrating in a sound wave. However, a particle of air is something indefinite. Therefore, sound energy is given per unit of volume. This magnitude can be called the density of sound energy.

Since the mass of a unit of volume is the density ρ, the density of sound energy

$$w = \frac{\rho v_{\max}^2}{2}$$

Above we have spoken about another important physical quantity which vibrates according to the sinusoidal law with the same frequency as the speed. This is the sound, or excess, pressure. Since these quantities are proportional, we can say that the energy density is proportional to the square of the amplitude of sound pressure.

The maximum value of the speed of sound vibration for loud conversation is equal to 0.02 cm/s. One cubic centimetre of air weighs about 0.001 g. Therefore, the energy density is equal to

$$\frac{1}{2} \times 10^{-3} \times 0.02^2 \text{ erg/cm}^3 = 2 \times 10^{-7} \text{ erg/cm}^3$$

Suppose that a source is emitting sound. It is radiating sound energy in the surrounding air. It is as though the energy were "flowing" from the vibrating body. During a second, a definite amount of energy flows through each area element, which is perpendicular to the direction of the propagation of the sound. This quantity is called the *energy flux* passing through the area element. Furthermore, if we take an area element of 1 cm², the amount of energy which has passed through it is called the *intensity of the sound wave*.

It is not difficult to see that the intensity I of sound is equal to the product of the energy density w by the speed of sound c. Imagine a small cylinder of 1-cm height and 1-cm² base area whose generatrices are parallel to the direction of propagation of a sound. The energy w contained in such a cylinder will completely leave it during a time of $1/c$. Therefore, an energy of $w/(1/c)$, i.e. wc, will pass through a unit of area during a unit of time. It is as though the energy were moving with the speed of sound.

During a loud conversation, the intensity of the sound near the talkers will be approximately equal to (we are making use of the number obtained above)

$$2 \times 10^{-7} \times 3 \times 10^{4} = 0.006 \text{ erg/cm}^2\cdot\text{s}$$

Audible and Inaudible Pitches

But what sounds can be perceived by the human ear? It turns out that the ear is capable of perceiving only the vibrations lying within the interval from approximately 20 to 20 000 Hz. Sounds with a arge frequency are called high-pitched, and those with a small frequency low-pitched.

But what wavelengths correspond to the limiting audible frequencies? Since the speed of sound is approximately equal to 300 m/s, using the formula $\lambda = cT = c/\nu$, we find that the lengths of audible pitches corresponding to wavelengths that lie within the limits of 15 m for the lowest tones to 3 cm for the highest ones.

And how do we "hear" these vibrations?

The way the organ of hearing functions has not as yet been fully clarified. The crux of the matter is that the internal ear (the cochlea, a canal of few centimetres long and filled with fluid) contains several thousand sensory nerves capable of perceiving sound vibrations transmitted to the cochlea from the air through the tympanic membrane. This or that part of the cochlea vibrates more strongly depending on the frequency of sound. Although the sensory nerves are situated along the cochlea so closely that a large number of them are stimulated simultaneously, man (and animals) is capable, particularly in childhood, of distinguishing minute changes in frequency (thousands of a fraction). It is still not known precisely just how this occurs. The only obvious fact is that the analysis by the brain of the stimuli arriving from many different nerves is of utmost importance here. A mechanical model of the same design as the human ear that could be capable of discerning sound frequencies just as well has yet to be invented.

A sound frequency of 20 000 Hz is the value beyond which the human ear does not perceive the mechanical vibrations of a medium. It is possible to create vibrations of a higher frequency in various ways; a person will not hear them, but instruments can record them. Incidentally, not only instruments record such vibrations. Many animals—bats, bees, whales and dolphins (as can be seen, it isn't a question of the dimensions of a living being)—are capable of perceiving mechanical vibrations with frequencies up to 100 000 Hz.

We are now able to obtain vibrations with frequencies up to a thousand million hertz. Such vibrations, although of inaudible pitch, are called *ultrasonic* or *supersonic* in order to affirm their affinity to sound. Supersounds of the highest frequencies are obtained with the aid of quartz plates. Such plates are cut out of monocrystals of quartz.

7. Transformations of Molecules

Chemical Reactions

Physics is the foundation of all natural sciences. It is therefore absolutely impossible to separate physics from chemistry, geology, meteorology, biology and all the other branches of science. The basic laws of nature come under the topic of physics. It is no mere chance then that books have been written on geological physics, biological physics, chemical physics, construction physics, etc. Hence, we find it appropriate to devote a section to chemical reactions in this book which deals with the basic laws of nature.

Strictly speaking, chemistry begins where a molecule is broken down into its component parts, or when a single molecule is formed of two others, or when two colliding molecules are converted into two other molecules. If we find that from the beginning to the end of a phenomenon a change has occurred in the chemical composition of the bodies involved, then a reaction has taken place.

Chemical reactions can occur "on their own", i.e. due to the motions of the molecules at the given temperature. Hence, we often say that a substance decomposes. This means that the internal vibrations of the atoms in the molecules rupture the bonds between the atoms and the molecule "falls apart".

A chemical reaction is most often the result of encounters between molecules. A metal rusts. This is a chemical reaction: an atom of the metal encounters a molecule of water, and an oxide is formed. A pinch of citric acid and a spoon of soda are mixed into a glass of water. Bubbles of gas begin to evolve vigorously. The encounter of these two kinds of molecules has resulted in the formation of new substances, including carbon dioxide whose bubbles rise to the surface and burst.

Hence, spontaneous disintegration of molecules and collision of molecules are two causes of chemical reactions.

But chemical reactions may be due to other causes as well. You are vexed when you examine the suit of clothes that you took along on your vacation trip to the south. The cloth has faded and lost its true colour. Owing to intense action of the Sun's rays, a chemical transformation has occurred in the dye.

Reactions induced by light are said to be photochemical. Investigations in this field must be especially carefully conducted to distinguish heat-induced reactions, due to heat generated by light (which increases the kinetic energy of motion of molecules so that their collisions are more frequent and more violent), from reactions directly induced by light. In the latter, particles of light—photons—"rupture" the chemical bonds.

The action of light is responsible for the chain of chemical reactions that take place in green plants, and which is called photosynthesis. The photochemical transformation occurring in living plants realizes the great carbon cycle without which life would be impossible.

Chemical bonds may be ruptured in various chemical reactions by other energetic particles as well, such as electrons, protons, etc.

Chemical reactions may proceed either with the absorption of heat or with its evolution. What does this signify at the molecular level? If two slow molecules meet and form two fast ones, then heat has been generated because we know that an increase in temperature is equivalent to an acceleration of the molecules. Such reactions include combustion and explosion, which we are to discuss in the next section.

Next we shall consider the reaction rate from the molecular point of view, i.e. at the molecular level. Just about everyone knows that some reactions are completed faster than you can blink an eye (say, explosions), while others take years. Assume that we are again concerned with reactions in which two molecules collide and form two other molecules. The following assumption is evidently true. Of significance, in the first place, is collision energy of an amount sufficient to break up the molecules and to rearrange them. Also important, in the second place, is whether the reaction proceeds regardless of the angle at which the molecules meet in collision or whether they must meet at certain angles.

The minimum energy required to implement a reaction is called the *activation energy*. It plays the chief role in the course of the reaction, but we must give its due to a second factor as well—the percentage of "lucky" collisions of particles having a given energy.

A heat-producing chemical reaction can be modelled as shown in Figure 7.1. The ball rolls uphill, over the barrier and drops down. Since the initial energy level is higher than the final one, more energy is produced than has been expended.

This mechanical model visually illustrates the critical dependence of the reaction rate on the temperature. If the temperature is low, the "speed" of the ball is insufficient to surmount the barrier. As the temperature increases, the number of balls leaping over the barrier increases faster and faster. The rate of chemical reactions depends to an exceptionally great extent on the temperature. As a rule, a temperature increase of 10 degrees speeds up a reaction from two- to four-fold. If the reaction rate is, say, tripled when we raise the temperature 10 degrees, then a temperature increase of 100 degrees leads to a rate

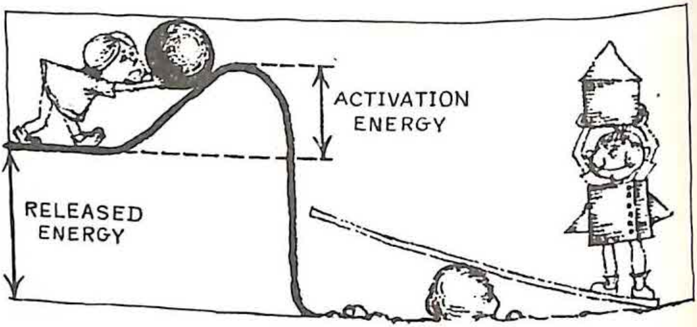

Figure 7.1

increase of $3^{10} \approx 60\,000$ times, 200 degrees to $3^{20} \approx 4 \times 10^{9}$, and 500 degrees to 3^{50}, i.e. approximately 10^{24} times. No wonder then that a reaction proceeding at a normal rate at 500 °C does not take place at all at room temperature.

Combustion and Explosion

For combustion to begin, it is necessary, as is well known, to bring a burning match to an inflammable object. But neither does a match light up by itself; it must be struck against a match-box. Therefore, in order that a chemical reaction start, a preliminary heating is necessary. The ignition creates the required temperature for the reaction at the initial moment. A high temperature is further maintained by the heat which is liberated in the course of the reaction.

The initial local heating should be sufficient for the heat liberated by the reaction to exceed that transferred to the cold surrounding medium. Therefore, each reaction has its own, as one says, *ignition point*. Combustion only begins if the initial temperature is higher than the

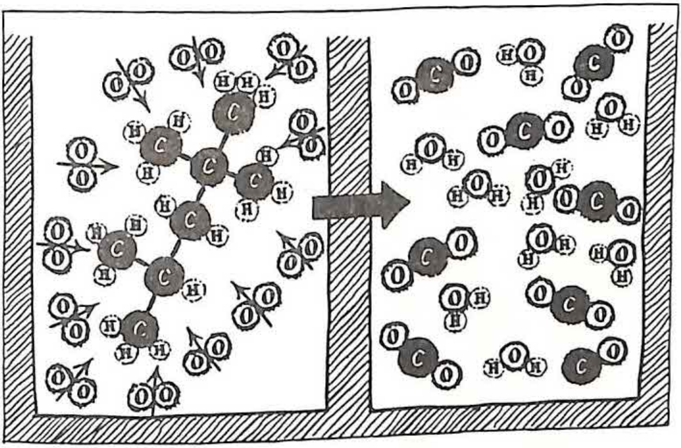

Figure 7.2

ignition point. For example, the ignition point of wood is 610 °C, of benzine about 200 °C, of white phosphorus 50 °C.

The combustion of wood, coal or oil is a chemical reaction uniting the substance with the oxygen of the air. Therefore, such a reaction proceeds at the surface: until the outside layer burns up, the next layer cannot participate in the combustion. This is what explains the relative slowness of such combustion. It is not difficult to convince oneself in practice of the validity of what we have said. If fuel is broken up into small pieces, the rate of combustion may be considerably increased. This is why the crushing of coal is carried out in furnaces.

Fuel fed to the cylinder of an internal-combustion engine is broken down and mixed with air in exactly the same way. More complex substances than coal are used for engine fuel, for instance, gasoline. A molecule of such a substance is shown in Figure 7.2 at the left. It consists of 8 carbon atoms and 18 hydrogen atoms bonded together as shown. As it burns, this molecule is subject to collisions from oxygen molecules. These collisions break up the gasoline molecules. The forces that join one or two carbon atoms to a hydrogen atom in a molecule, and those that join two oxygen atoms to make up an oxygen molecule, cannot withstand the stronger "affinity", as chemists say, between oxygen atoms, on the one hand, and carbon and hydrogen atoms, on the other. Consequently, the old bonds between the atoms in a molecule are ruptured and the atoms are rearranged into new molecules. As is indicated in Figure 7.2 at the right, the new molecules—combustion products—consist of carbon dioxide and water. Water is produced in the form of steam.

The situation is entirely different in the case where the atmosphere is not needed, where everything that is necessary for the reaction is contained within the substance. An example of such a substance is a mixture of hydrogen and oxygen (it is called a detonating gas). The reaction occurs not at the surface but within the substance. Unlike the case of combustion, all the energy forming in the course of the reaction is liberated almost instantaneously, as a result of which the pressure rises sharply and an explosion takes place. A detonating gas doesn't burn—it explodes.

Thus, an explosive should contain within it the atoms or molecules needed for a reaction. It is evident that we can prepare explosive gas mixtures. There also exist solid explosives. They are explosive precisely because in their compositions all atoms occur which are necessary for chemical reactions giving off heat and light.

The chemical reaction taking place during an explosion is a decomposition reaction of the splitting up of molecules into parts. An example of an explosive reaction is shown in Figure 7.3—the splitting up of a nitroglycerine molecule into its parts. As is evident from the right-hand

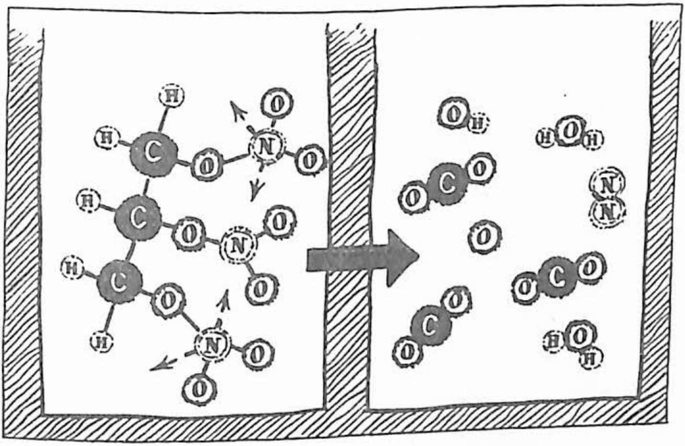

Figure 7.3

part of the diagram, molecules of carbon dioxide, water and nitrogen are formed out of the original molecule. We find the ordinary combustion products among the end products, but combustion has occurred without the participation of oxygen molecules from the air; all atoms necessary for the combustion are contained within the nitroglycerine molecule.

How is an explosion propagated through an explosive, for example, a detonating gas? When we set fire to an explosive, a local heating arises. A reaction occurs in the heated region. But heat is liberated in the course of the reaction, and passes into the adjacent layers of the mixture by means of heat transfer. This heat is sufficient for the reaction to take place in the neighbouring layer, too. New amounts of the heat being liberated enter the next layers of the detonating gas, and so with the rate of heat transfer the reaction spreads throughout the entire substance. The rate of such a transfer is of the order of

20-30 m/s. This is, of course, very rapid. A metre-long tube of gas explodes within one-twentieth of a second, i.e. almost instantaneously, while the rate of the combustion of wood or pieces of coal that takes place at the surface, and not within the volume, is measured in centimetres per minute, i.e. is several thousand times less.

Nevertheless, such an explosion may also be called slow, since a different kind of explosion, hundreds of times faster than the one described, is possible.

A shock wave gives rise to a fast explosion. If the pressure rises sharply in some layer of a substance, a shock wave will begin propagating from this place. A shock wave leads to a considerable jump in temperature which is transmitted from layer to layer. The rise in temperature gives an impetus to an explosive reaction, and the explosion leads to a rise in pressure and maintains the shock wave, whose intensity would otherwise fall off rapidly with its propagation. Therefore, a shock wave gives rise to an explosion, while the explosion in turn maintains the shock wave. The type of explosion described by us is called a detonation. Since a detonation is propagated through a substance with the speed of a shock wave (of the order of 1 km/s), it is actually hundreds of times faster than a "slow" explosion.

But which substances explode "slowly" and which explode "rapidly"? The question should not be posed in this fashion: one and the same substance can explode "slowly" and also detonate under different conditions, while a "slow" explosion turns into a detonation in certain cases.

Some substances, for example, nitrogen iodide, explode on contact with a straw, on being slightly heated or as a result of a flash of light. An explosive substance like trotyl does not explode when it is dropped or even shot out of a rifle. A powerful shock wave is required in order to explode it.

There exist substances even less sensitive to external influences. The fertilizing mixture of ammonium nitrate and ammonium sulfate had not been considered to be explosive until a tragic accident occurred in 1921 at a chemical factory in Oppau, Germany. An explosive method was used there for pulverizing mixtures which had become caked. As a result, a warehouse and the entire factory were blown up. The engineers at the factory could not be blamed for the catastrophe: approximately twenty thousand blasts had proceeded normally, and only once had the conditions favourable for detonation been created.

Substances which explode only when subjected to a shock wave but exist in a stable state and are not even afraid of fire under ordinary conditions are quite convenient for explosion technology. Such substances can be manufactured and stored in large amounts. However, in order to bring these inert explosives into action, initiators of the explosion are needed. Such initiating explosives are absolutely necessary as sources of shock waves.

Mercury fulminate can serve as an example of initiators. If a grain of it is placed on a sheet of tin and lighted, an explosion takes place, making a hole in the tin. An explosion of such a substance under any conditions is a detonation.

If a bit of mercury fulminate is placed on the charge of a secondary explosive and lighted, the explosion of the initiator creates a shock wave which is enough to detonate the secondary explosive. Explosions are produced in practice with the aid of a detonating capsule (1-2 g of an initiator). The capsule can be ignited at a distance, for example, with the aid of a long cord (Bickford fuse); the shock wave coming from the capsule will blow up the secondary explosive.

In a number of cases arising in technology, we must contend with detonations. "Slow explosions" of a mixture of gasoline and air occur in the motor of a car under ordinary conditions. However, sometimes a detonation also arises. Shock waves in a motor are absolutely unacceptable as a systematic phenomenon, since they will soon put the walls of the cylinders of the motor out of commission.

In order to cope with detonations in engines, it is necessary to either use a special gasoline with a high octane number or else mix the gasoline with special substances, antiknocks, which do not let a shock wave develop. One of the most widespread antiknocks is tetraethyl lead (TEL). This substance is highly toxic, and so drivers are warned of the need to be careful when using such gasoline.

Cannons must be constructed so as to avoid detonations. Shock waves should not be formed inside the barrel when the gun is being fired, otherwise, the gun will be put out of commission.

Engines Operated by Transformations of Molecules

People living in the 20th century use a great variety of engines and motors to help them do their work and to increase their power about ten-fold.

In the simplest case, it may prove expedient to convert mechanical energy into another kind of mechanical energy. For instance, we may have the wind or a stream of water rotate the vanes of a windmill or the water wheel of a mill.

In a hydroelectric power station, the process of converting the energy of a stream of water into rotary motion of the turbine runner is an intermediate one. The turbine drives an electrical machine, called a generator, which produces electricity. Such conversion of energy will be discussed further on.

Steam engines have become things of the past. A steam locomotive is fast becoming a rarity to be exhibited in museums. This has occurred because the efficiency of a heat engine is much too low.

This does not imply that steam turbines have become obsolete. But there as well the conversion of the energy of expanding steam into mechanical motion of the rotor is only an intermediate stage. The final stage is the production of electrical power.

As to aircraft and automobiles, there is obviously no point in powering them with a steam boiler or steam turbine. The total weight of the engine and heating device proves too great when calculated on a kilograms per horse power basis.

We can, however, eliminate the separate heating plant. In a gas turbine, the immediate working fluid consists of the incandescent combustion products of a high-energy fuel. In such engines, we use chemical reactions, i.e. transformations of molecules, to produce mechanical energy. This is what determines both the significant advantages of gas turbines over the steam-powered type, and the great design and manufacturing difficulties that have to be overcome to ensure their reliable performance.

The advantages are obvious: the combustion chamber, where the fuel is burned, has a small size and can be placed under the casing of the turbine. The components of combustion consisting, for example, of atomized kerosene and oxygen have a temperature unattainable for steam. The heat flow formed in the combustion chamber of a gas turbine is very intense, which makes it possible to obtain a high efficiency.

But these advantages turn into shortcomings. The steel blades of the turbine function in streams of gas having a temperature up to 1200 °C and inevitably saturated with microscopic ash particles. It is easy to imagine what great demands have to be made of the materials out of which gas turbines are manufactured.

During an attempt to construct a gas turbine with a power of about 200 hp for an automobile, it became necessary to deal with quite a peculiar difficulty: the turbine was of such small dimensions that the usual engineering solutions and the customary materials simply could not be used. However, the technological difficulties are already being overcome. The first automobiles powered by gas turbines have been designed and built, but it is difficult to foresee their future.

It turned out easier to utilize the gas turbine in railway transport. Locomotives with gas turbines, gas-turbine locomotives, have already received universal recognition.

But entirely different engines in which the gas turbine is a subordinate although necessary component part paved the way for the widespread use of the gas turbine. We are speaking of the turbojet engine, the basic type of engine at the present time in jet aviation.

The principle on which the jet engine is based is simple. A gas mixture is burned in a durable combustion chamber; the combustion products, having an extraordinarily great speed (3000 m/s, when hydrogen is burned in oxygen, somewhat less for other types of fuel), are thrust through a smoothly expanding nozzle in the direction opposite to that of motion. Even relatively small amounts of combustion products will carry a large momentum away from the engine.

With the creation of jet engines, people received the realistic opportunity of carrying out interplanetary flights.

Liquid propellant rocket engines have become very widespread. Definite portions of a fuel (for example, ethyl alcohol) and an oxidizer (usually liquid oxygen) are injected into the combustion chamber of such an engine. The mixture burns, creating traction. In high-altitude rockets, such as the V-2, the traction is of the order of 15 tonf. The figures are sufficiently eloquent: 8.5 tons of fuel and oxidizer which take 1.5 minutes to burn up are poured into the rocket. The use of liquid propellant rocket engines is only expedient for flights at great heights or beyond the Earth's atmosphere. It makes no sense to pour large amounts of a special oxidizer into an aircraft destined for flights in the lower layers of the atmosphere (up to 20 km), where there is enough oxygen. But then the problem arises of forcing huge amounts of air necessary for intensive burning into the combustion chamber. This problem is solved in a natural fashion: part of the energy of the gas stream created in the combustion chamber is taken away to rotate the powerful compressor forcing air into the chamber.

We have already said what engine can do work at the expense of the energy of a stream of incandescent gases; of course, this is the gas turbine. The whole system is called a turbojet engine (Figure 7.4). A turbojet engine has no competitor for flights with speeds from 800 to 1200 km/h.

For long-distance flights with speeds of 600-800 km/h an ordinary aircraft propeller is added to the shaft of a turbojet engine. This is a turboprop engine.

At flying speeds of about 2000 km/h or more, the air pressure developed by the aircraft is so great that the need for a compressor no longer arises. It is then only natural that neither is a gas turbine needed. The engine is converted into a pipe of variable cross-section, in which fuel is burned at a very definite place. This is a ramjet engine. It is clear that a ramjet engine cannot lift an aircraft off the ground: it becomes capable of functioning only at very high flying speeds.

Jet engines are completely inexpedient for flights at small speeds owing to the large expenditures of fuel.

For motion on land, on water or in air with speeds from

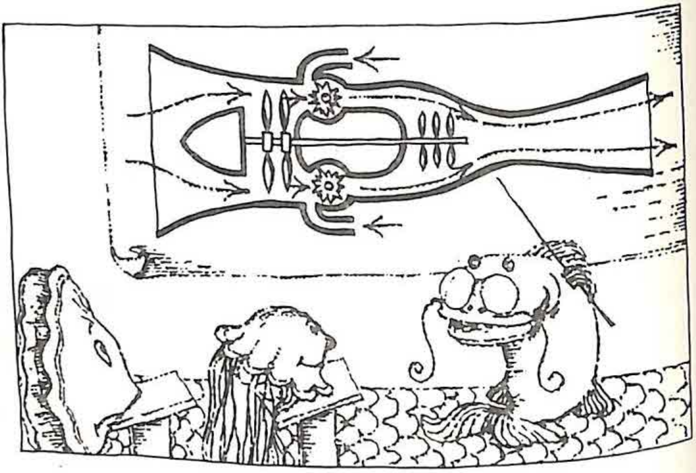

Figure 7.4

0 to 500 km/h, people are reliably served by gasoline or diesel internal-combustion piston engines. As indicated by the name, the main part of such an engine is the cylinder inside which the piston can move. The back-and-forth motion of the piston is transformed into a rotary motion of the shaft with the aid of the connecting rod and crank system (Figure 7.5).

The motion of the piston is transmitted through the connecting rod to the crank, which is part of the crankshaft. The motion of the crank sets the shaft into rotation. Conversely, if the crankshaft is turned, this will move the connecting rods and a displacement of the pistons inside the cylinders will set in.

The cylinder of a gasoline engine is equipped with two valves, one of which is meant for the inlet of the fuel mixture, and the other for the exhaust of waste gases. In order to start the engine, we must turn it over, using

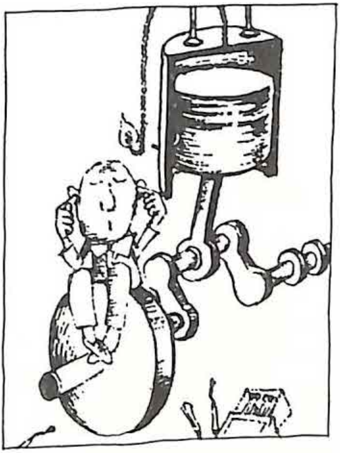

Figure 7.5

the energy of some outside source. Assume that at a certain moment the piston is moving down and the inlet valve is open. A mixture of atomized gasoline and air is sucked into the cylinder. The inlet valve is connected to the shaft of the engine in such a way that it closes at the moment when the piston reaches its lowest position. As the shaft continues to turn, the piston starts coming up. The automatic drive of the valves keeps then closed during this stroke, and the fuel mixture is therefore compressed. When the piston reaches its highest position, the compressed mixture is ignited by an electric spark, which jumps between the electrodes of the spark plug. The mixture ignites and the expanding combustion products act, pushing the piston down. The engine shaft receives a powerful thrust, and the flywheel on the shaft stores considerable kinetic energy. All of the next three preliminary strokes proceed at the expense of this energy: first the exhaust, when the exhaust valve is open and the piston is moving up, driving the exhaust out of the cylinder, next the intake and compression that we already know about, then a new ignition. The engine is started.

Gasoline engines have powers from fractions of a horsepower to 4000 hp, an efficiency of up to 40% and weigh up to 300 gf per horsepower. Their widespread utilization in automobiles and aircrafts is explained by such a good showing.

How might we increase the efficiency of a gasoline engine? The major means is by raising the degree of compression.

If the fuel mixture is more highly compressed before ignition, it will have a higher temperature. And why is it of advantage to raise its temperature? The point is that we can rigorously prove that the maximum attainable efficiency equals $1-T/T_0$, where T is the temperature of the working body, and T_0 is the ambient temperature. This proof is tedious and uninteresting, and we omit it. In numerous instances we have asked our readers to just take our word for various statements. Since the ambient temperature, i.e. the temperature of the surrounding medium, is something we cannot do much about, we make every effort to raise the temperature of the working body as high as is feasible. But—there, unfortunately, is a but—a highly compressed fuel mixture detonates (see p. 204). Then the working stroke acquires the features of a heavy explosion which may damage the engine.

One has to take special measures to decrease the detonation properties of the gasoline, and this would greatly raise the cost of a fuel that is already quite expensive.

The problems of raising the temperature during the working stroke, of eliminating detonation and reducing the cost of the fuel have been successfully solved in the diesel engine.

A diesel engine resembles a gasoline engine to a great extent in its construction, but is designed for products of oil distillation which are cheaper than and inferior in quality to gasoline.

The cycle begins with the admission of pure air into the cylinder. The air is then compressed by the piston to approximately 20 atm. It would be very difficult to achieve such a high compression by turning over the engine by hand. Therefore, diesel engines are started with a special starting motor, usually a gasoline one, or by compressed air.

When highly compressed, the temperature of the air in a cylinder rises so much that it becomes sufficient for the fuel mixture to ignite. But how can it be admitted into the cylinder, where a high pressure has been attained? An inlet valve would not be suitable here. It is replaced by a sprayer which forces the fuel into the cylinder through a tiny opening. It ignites as it enters, eliminating the danger of a detonation considerable for a gasoline engine.

Eliminating the danger of a detonation permits us to construct slow diesels with many thousands of horsepowers. Naturally, they acquire quite considerable dimensions, but remain more compact than an aggregate consisting of a steam boiler and a turbine.

A ship in which there are direct-current generator and motor between a diesel engine and a blade is called a diesel-electric motor ship.

Diesel locomotives, now being widely introduced on railroads, are built along the same lines; they may in a sense be called diesel-electric locomotives.

Internal-combustion piston engines, considered last by us, have borrowed their basic constructive elements—the cylinder, the piston, the connecting rod and crank mechanism which helps obtain rotary motion—from the steam engine, now gradually leaving the scene. The steam engine could have been called an "external-combustion piston engine". It is precisely this combination of the unwieldy steam boiler with the no less unwieldy system of transforming translatory motion into rotary one that deprives the steam engine of the possibility of successfully competing with more modern engines.

Modern steam engines have an efficiency of about 10%. The locomotives which have been taken out of production released up to 95% of the fuel they burned through the smoke-stack to no advantage.

This "record-breaking" low efficiency is explained by the inevitable deterioration in the properties of a steam boiler designed for installation on locomotive as compared to a stationary steam boiler.

But why were steam engines employed so widely in transportation for such a long time? Besides adherence to customary solutions, the circumstance that a steam engine has a very good tractive characteristic also played a role: the greater the force with which the load resists a displacement of the piston, the greater the force exerted on it by the steam, i.e. the torque developed by a steam engine grows under difficult conditions, which is important in transportation. But, of course, the fact that the steam engine does not need a complicated system of variable transmission to the driving axles cannot in the least compensate for its basic defect, a low efficiency. This is what explains the supplanting of the steam engine by other engines.

8. Laws of Thermodynamics

Conservation of Energy at the Molecular Level

The laws of thermodynamics belong to the basic laws of nature. There are not many such laws. You can count them on the fingers of one hand.

The chief aim of science, including physics, of course is the search for the rules, regularities, general laws and the basic laws that govern nature. This search begins with observations or experiments. That is why we say that all of our knowledge is of an empirical or experimental nature. Investigations and observations are followed by a search for generalization. Persistent brain work, meditation, calculations and inspiration enable us to find laws of nature. Next comes the third stage: from the general laws, we derive, in a strictly logical manner, the ensuing effects and special laws that can be checked by experiments. This, by the way, is what the explanation of a phenomenon consists of. To explain means to correlate the particular with the general law.

A cherished goal of science has been, of course, successful attempts to reduce laws to the minimum number of postulates. Physicists tirelessly search for such opportunities; they seek to express the whole sum of knowledge about nature in several concise and elegant formulas. Albert Einstein tried for about thirty years to unify the laws of gravitational and electromagnetic fields. The future will show whether or not this proves possible.

What, then, are these laws of thermodynamics? Too brief a difinition must necessarily be somewhat inaccurate. Maybe we approach the essence of the matter closest of all if we contend that *thermodynamics* is a study of the rules according to which bodies exchange energy. The laws of thermodynamics enable us to find strictly logical relations by mathematical means between the thermal and mechanical properties of bodies, and to establish a number of vital principles concerned with the change of state of bodies. Perhaps, the most precise definition of the branch of physics we are about to give our attention to is the trivial statement: thermodynamics is the totality of knowledge that follows from the first and second laws of thermodynamics.

The first law of thermodynamics was formulated in a concise and expressive form back in the time when physicists preferred not to mention molecules. Such a formulation (which does not require us to "get inside" a body) is said to be phenomenological, i.e. one simply referring to the phenomena. The first law of thermodynamics constitutes a certain refinement and expansion of the energy conservation law.

We have established that a body has kinetic and potential energies, and that in a closed system, the sum of these energies—the total energy—can neither be destroyed nor created. Energy is conserved.

Except with respect to the motion of celestial bodies, we can contend without exaggeration that there are no phenomena in which mechanical motion is not accompanied with heating or cooling surrounding bodies. When a body is stopped by friction, its kinetic energy would seem, on the face of it, to be lost. This first impression is misleading, however. Actually, it can be proved that conservation is maintained with absolute precision: the mechanical energy of the body has been utilized to heat the surrounding medium. What does this mean at the molecular level? Simply that the kinetic energy of the body has been transformed into kinetic energy of molecules.

This seems clear enough, but what happens when we crush ice in a mortar with a pestle? We keep pounding and the thermometer reading remains at zero all the time. It would seem that the mechanical energy we exert has vanished. If not, what has happened to it? Again, we find a clear answer: the ice has been converted into water. This means that the mechanical energy was expended in rupturing the bonds between the molecules, and their internal energy has been changed. Each time we observe that the mechanical energy of a body has disappeared, we readily discover that this only seems to be so, and that actually mechanical energy has been converted into the internal energy of the bodies being observed.

In a closed system, certain bodies can lose and others can gain internal energy. But the sum of the internal energies of all the bodies added to their mechanical energies remains constant for the given system.

Now let us turn our attention away from mechanical energy. We consider two instants in time. At the first instant, the bodies were at rest, then certain events occurred, and at the second instant the bodies are again at rest. We are certain that the internal energy of all the bodies in the system remained constant. But some bodies have lost and others have acquired energy. This could happen in two ways. Either one body performed mechanical work on another (for example, by compressing or stretching it), or one body transferred heat to another body.

The first law of thermodynamics states that the change in the internal energy of a body is equal to the sum of the work done on the body plus the heat transferred to it.

Heat and work are two different forms in which energy can be transferred from one body to another. Heat exchange is accomplished by disordered collisions of molecules. Mechanical energy is transmitted with the molecules of one body aligned in orderly "rows and ranks" transferring their energy to another body.

How Heat Is Converted into Work

The word "heat" in this heading has been employed somewhat carelessly. As mentioned immediately above, heat is a form of energy transfer. Consequently, a more proper formulation of the question would be: How to convert thermal energy, i.e. kinetic energy of molecular motion, into work. But the word "heat" is customary, concise and expressive. We hope the reader will not be confused if we continue to apply the word in the sense we have just accurately defined.

There is certainly plenty of heat around us. But, unfortunately, all of this energy of molecular motion is absolutely useless insofar as it cannot be converted into work. Such energy cannot be ranked in any way among our energy resources. Let us look into this matter.

A pendulum which has been deflected from its equilibrium position will sooner or later come to rest, a wheel of an upside-down bicycle, which has been spun by hand, will make a lot of turns, but it, too, will eventually stop moving. There is no exception to the following important law: all the spontaneously moving bodies surrounding us will eventually come to rest.*

If there are two bodies, one heated and the other cold, heat will be transferred from the former to the latter until their temperatures are equalized. Then the heat transfer will cease and the states of the bodies will stop changing. Thermal equilibrium will set in.

There is no phenomenon whereby a body spontaneously leaves a state of equilibrium. A wheel on an axle at rest never starts turning by itself. Neither does it happen that an ink-well on a table warms up by itself.

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*Here, of course, we do not have in mind a uniform translatory motion or a uniform rotation of a system of bodies as a whole.

The tendency towards equilibrium implies that events take a natural course: heat passes from a hot body to a cold one, but cannot spontaneously pass from a cold body to a hot one.

As a result of air resistance and friction at the suspension, the mechanical energy of an oscillating pendulum will be converted into heat. However, not under any conditions will a pendulum begin swinging at the expense of the heat of the surrounding medium. Bodies come to a state of equilibrium, but cannot leave it spontaneously.

This law of nature shows at once what part of the energy surrounding us is absolutely useless. This is the energy of the thermal motion of the molecules of those bodies which are in a state of equilibrium. Such bodies are incapable of converting their energy into mechanical motion.

This part of the energy is immense. Let us calculate the value of this "inaccessible" energy. If the temperature is lowered by one degree, then a kilogram of earth, having a heat capacity of 0.2 kcal/kg, loses 0.2 kcal. A relatively small figure. However, let us estimate how much energy we would obtain if we were able to cool by only one degree a substance with the mass of the Earth, i.e. 6×10^{24} kg. Multiplying we obtain an immense figure: 1.2×10^{24} kcal. In order that you might picture this value, let us state at once that at the present time, the yearly energy output of all the electric power stations in the world is equal to 10^{15}-10^{16} kcal, i.e. about a thousand million times less.

We needn't be astonished by the fact that such calculations act hypnotically on poorly informed inventors. We have spoken above of attempts to construct a perpetual motion machine ("perpetuum mobile") creating work out of nothing. Operating with the principal propositions of physics following from the law of conservation of energy, one cannot possibly refute this law with the creation of a perpetual motion machine (we shall now call it a *perpetual motion machine of the first kind*).

The same sort of error is also committed by certain cleverer inventors, who create models of machines performing mechanical motion at the expense of nothing but by cooling the medium. Such, alas, unrealizable machines are called *perpetual motion machines of the second kind*. Here, too, a logical error is committed, since the inventor bases himself on laws of physics, which are consequences of the law by which all bodies tend towards a state of equilibrium, and with the aid of these laws, tries to refute the foundations on which they are based.

Thus, it is impossible to produce work by merely taking heat from a medium. In other words, a system of bodies in equilibrium with each other is energetically barren.

Hence, in order to obtain work, it is first of all necessary to find bodies which are not in equilibrium with their neighbours. Only then will one succeed in realizing a process of transferring heat from one body to another or converting heat into mechanical energy.

The creation of an energy flux is a necessary condition for obtaining work. In the "path" of such a flux a conversion of some of the energy of bodies into work is possible. Therefore, the energy of only those bodies which are not in equilibrium with the surrounding medium is ranked among the energy reserves which are of use to people.

The law which we have just expounded, the impossibility of building a perpetual motion machine of the second kind, is called the second law of thermodynamics. So far we have expressed it in the form of a phenomenological rule. But since we know that bodies consist of molecules and that the internal energy is the sum of the kinetic and potential energies of the molecules, the sudden appearance of some kind of "additional" law may seem strange. Why is the law of conservation of energy formulated for molecules insufficient to explain all phenomena in nature?

In short, this poses the following question: Why do molecules behave so that when left to themselves they tend towards a state of equilibrium?

Entropy

This question is very important and interesting. In order to answer it, we will have to begin from afar.

Frequently encountered events that occur at every turn are said to be highly probable. On the contrary, events that occur thanks to a rare coincidence are regarded as improbable.

An improbable event does not require a display of any supernatural forces whatsoever. There is nothing impossible about it, nothing contradicting the laws of nature. And nevertheless, in many cases we are perfectly sure that the improbable is identical with the impossible.

Consider a lottery prize-list. Count the number of winning tickets whose numbers end with a 4, 5 or 6. You will not be the least bit surprised when you find that approximately one-tenth of the winning tickets correspond to each digit. Well, but perhaps tickets with numbers ending with a 5 were to make up one-fifth of the winners, instead of one-tenth? Unlikely, you say. Well, and if half of the winning tickets were to have such numbers? No, that would be absolutely improbable ..., and therefore, also impossible.

Reflecting on what conditions are necessary for an event to be probable, we arrive at the following conclusion: the probability of an event depends on the number of ways in which it can be realized. The greater this number, the more frequently will such an event occur.

More precisely, the *probability* is the ratio of the number of ways of realizing a given event to the number of ways of realizing all possible events.

Write down the numbers from 0 to 9 on ten cardboard discs and place them in a sack. Now pull out a disc, note its number and put it back in the sack. This is very much like a lottery drawing. It can be confidently said that you will not draw one and the same number, say, seven times in a row, even if you devote an entire evening to this boring occupation. Why? The drawing of seven identical numbers is an event which is realizable in only ten ways (7 zeros, 7 ones, 7 twos, etc.). But there are a total of 10^7 possible ways of drawing seven discs. Therefore, the probability of drawing seven discs in a row with identical numbers is equal to $10/10^7 = 10^{-6}$, i.e. only one-millionth.

If black and white grains are poured into a box and mixed with a shovel, the grains will very soon be distributed uniformly throughout the entire box. Scooping up a handful of grains at random, we shall find approximately the same number of white and black grains in it. No matter how much we mix them, the result will always be the same—uniformity is preserved. But why doesn't the separation of the grains take place? Why won't we succeed in driving the black grains to the top and the white grains to the bottom by means of a prolonged mixing? Here, too, it is entirely a matter of probability. The state in which the grains are distributed disorderly, i.e. black and white grains are uniformly intermingled, can be realized in an enormous number of ways and, consequently, possesses the greatest probability. On the contrary, the state in which all the white grains are on the top and all the black grains at the bottom is unique. Therefore, the probability of its realization is negligibly small.

We can easily pass from grains in a sack to the molecules that bodies are made of. The behaviour of molecules is subject to chance. This can be seen particularly clearly in the case of gases. As we know, gas molecules collide randomly and move in all possible directions, first with one speed and then with another. This eternal thermal motion continually reshuffles the molecules, mixes them like a shovel mixes the grains in a box.

The room in which you are now is filled with air. Why can't it happen at some moment that the molecules in the lower half of the room pass into the upper half—under the ceiling? Such a process is not impossible—it is very improbable. But what does very improbable mean? If such a phenomenon were even a thousand million times less probable than a disordered distribution of molecules, someone might nevertheless observe it. Will we really observe such a phenomenon?

A computation shows that such an event for a 1-cm^3 vessel in volume takes place once in $10^{3\times10^{19}}$ cases. It hardly pays to make a distinction between the words "extremely improbable" and "impossible". For the number written above is unimaginably great; if we divide it by the number of atoms not only on the Earth but also in the entire solar system, it will still remain enormous.

But what will the state of the gas molecules be? The most probable one. And the most probable state will be that which is realizable in the greatest number of ways (the molecules will all be distributed at random) for which there are approximately the same numbers of molecules moving to the right as to the left, upwards as downwards, for which one finds identical numbers of molecules in equal volumes, the same proportion of fast and slow molecules in the upper and lower halves of the vessel. Any deviation from such a disorder, i.e. from the random intermingling of molecules with respect to position and velocity, is linked with a decrease in probability, or, more concisely, is an improbable event.

On the contrary, phenomena linked with an intermingling, with the creation of disorder out of order increase the probability of state. Hence, it is these phenomena that will determine the natural course of events. The law of the impossibility of a perpetual motion machine of the second kind and the law by which all bodies tend towards an equilibrium state receive their explanation. Why is mechanical motion transformed into thermal? Simply because mechanical motion is ordered and thermal is disordered. The transition from order to disorder increases the probability of state.

Physicists called the quantity characterizing the degree of order and related by a simple formula to the number of ways of creating states *entropy*. We shall not give the formula, but shall only say that the greater the probability, the greater the entropy.

The law of nature which we are now discussing asserts: all natural processes proceed in such a way that the probability of state increases. In other words, this same law of nature can be formulated as the law of increasing entropy.

The law of increasing entropy is one of the most important laws of nature. From it follows, in particular, the impossibility of constructing a perpetual motion machine of the second kind, or, which is the same, the assertion that bodies left to themselves tend to a state of equilibrium. The law of increasing entropy is the same second law of thermodynamics. Only its formulation is different, but its content is the same. What is more important is that we have given an interpretation of the second law of thermodynamics at the molecular level.

In a certain sense, the union of these two laws "under a single banner" was quite fortunate. For the law of conservation of energy is an absolute law. But as for the law of increasing entropy, as follows from what has been said above, it is applicable only to sufficiently large collections of particles and is simply impossible to formulate for individual molecules.

The statistical (this means pertaining to a large collection of particles) character of the second law of thermodynamics does not in the least diminish its significance. The law of increasing entropy predetermines the direction of processes. In this sense, entropy may be called the managing director of natural resources, while energy serves as its bookkeeper.

Fluctuations

We have seen that spontaneous processes bring a system to its most probable state, i.e. to the growth in entropy. After the entropy of a system has become maximum, equilibrium is reached.

But a state of equilibrium does not by any means imply internal rest. An intensive thermal motion takes place within the system. Therefore, strictly speaking, any physical body "stops being itself" at each instant: the mutual distribution of its molecules at every successive moment is not the same as it was at the preceding one. Consequently, the values of all physical quantities are conserved only "on the average"; they are not exactly equal to their most probable values, but vary around them. Deviations from the most probable values at equilibrium are called *fluctuations*. The values of the various fluctuations are extremely negligible. The greater the value of a fluctuation, the less probable it is.

The average value of a relative fluctuation, i.e. the fraction of the magnitude of the physical quantity of interest by which it can change as a result of the chaotic thermal motion of molecules, can be approximately represented by the expression $1/\sqrt{N}$, where N is the number of molecules in the body, or in that part of it, which we are investigating. Therefore, fluctuations are appreciable for systems consisting of a small number of molecules, and completely insignificant for large bodies containing millions of millions of millions of molecules.

The formula $1/\sqrt{N}$ shows that in one cubic centimetre of a gas, the density, pressure, temperature and also any other properties can change by $1/\sqrt{3 \times 10^{19}}$, i.e. by not more than 10^{-8}%. Such fluctuations are too small to be detected experimentally. However, things are entirely different for a volume of a cubic micrometre. Here $N = 3 \times 10^7$ and fluctuations will attain measurable values of the order of hundredths of a per cent.

A fluctuation is an "abnormal" phenomenon in the sense that it implies a transition from a more probable state to a less probable one. In the course of a fluctuation, heat transfers from a cold body to a hot one, the uniform distribution of molecules is violated and an ordered motion sets in.

Will someone perhaps succeed in constructing a perpetual motion machine of the second kind on the basis of these violations?

Let us imagine, for example, a tiny turbine placed in a rarefied gas. Can't we arrange things in such a way that this small machine would react to all fluctuations in an arbitrary but fixed direction? For example, so that it would rotate if the number of molecules flying to the right became greater than the number of molecules moving to the left? Such small tremors might be accumulated, eventually giving rise to work. The law asserting the impossibility of a perpetual motion machine of the second kind would be refuted.

But, alas, such a mechanism is impossible in principle. A detailed examination, taking into account the fact that the turbine would have its own fluctuations (the greater, the smaller its dimensions), shows that fluctuations can never perform any work whatsoever. Although violations of the tendency towards equilibrium continually arise around us, they cannot change the inexorable course of physical processes in the direction increasing the probability of state, i.e. entropy.

Who Discovered the Laws of Thermodynamics?

Here it is impossible to limit ourselves to a single name. The second law of thermodynamics has its own history. Here, too, just as in the history of the first law of thermodynamics, the name of the Frenchman Sadi Carnot should be mentioned first of all. In 1824, he published a work entitled *Reflections on the Motive Power of Fire* at his own expense. It was first demonstrated in this work that heat cannot pass from a cold body to a warm one without the consumption of work. Carnot also showed that the maximum efficiency of a heat engine is determined only by the difference in the temperatures of the heater and the cooling medium.

Only after Carnot's death in 1832 did other physicists pay attention to this work. However, it had little influence on the further development of science because all of Carnot's writings were based on the recognition of an indestructible and uncreatable "substance"—caloric.

Only after the work of Mayer, Joule and Helmholtz, who established the law of equivalence of heat and work, did the great German physicist Rudolf Clausius (1822-1888) arrive at the second law of thermodynamics and formulate it mathematically. Clausius introduced the concept of entropy and showed that the essence of the second law of thermodynamics can be reduced to the inevitable growth of entropy in all real processes.

The second law of thermodynamics permits one to formulate a number of general laws which all bodies should

Rudolf Clausius (1822-1888)—an outstanding German theoretical physicist. Clausius was the first to accurately formulate the second law of thermodynamics: in 1850, in the form of the thesis of the impossibility of heat being spontaneously transmitted from a colder body to a hotter one, and in 1865, with the aid of the obey, regardless of their structures. However, there still remains the problem of finding the relationship between the structure of a body and its properties. The branch of physics, which is called *statistical physics*, gives an answer to this question.

It is clear that in calculating physical quantities describing a system consisting of millions of millions of millions of particles, a new approach is absolutely necessary. In fact, it would be pointless, not to say completely impossible, to follow the motions of all the particles and describe this motion with the aid of formulas of mechanics. However, it is precisely this enormous number of particles which enables us to apply new "statistical" methods to the study of bodies. These methods widely use the concept of the probability of events. The foundations of statistical physics were laid down by the outstanding Austrian physicist Ludwig Boltzmann (1844-1906). In a series of papers, Boltzmann showed how the indicated program can be carried out for gases.

The statistical interpretation of the second law of thermodynamics given by Boltzmann in 1877 was the logical culmination of these investigations. The formula relating the entropy and probability of state of a system was carved out on Boltzmann's tombstone.

It would be difficult to overestimate the scientific achievement of Boltzmann, who discovered completely new paths in theoretical physics. Boltzmann's inves-

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concept of entropy which he introduced. Clausius was one of the first to consider the questions of the heat capacity of polyatomic gases and the thermal conductivity of gases. Clausius' work in the kinetic theory of gases contributed to the development of statistical concepts of physical processes. A series of interesting investigations into electrical and magnetic phenomena are due to Clausius.

tigations were subjected to ridicule during his lifetime by conservative German professors: at that time, atomic and molecular conceptions were regarded by many as naive. Boltzmann committed suicide, and the role played by the situation just described was undoubtedly far from the least important.

The edifice of statistical physics was perfected to a considerable degree by the work of the outstanding American physicist Josiah Willard Gibbs (1839-1903). Gibbs generalized Boltzmann's methods and showed how one might extend the statistical approach to all bodies.

Gibbs' last paper appeared at the beginning of the 20th century. A very modest researcher, Gibbs published his papers in the proceedings of a small provincial university. A considerable number of years had passed until his remarkable investigations were made known to all physicists.

Statistical physics has shown the way in which one can calculate properties of bodies consisting of a given number of particles. Of course, it should not be thought that these computational methods are all-powerful. If the nature of the motion of the atoms in a body is very complicated, as is the case for liquids, the actual computation becomes unfeasible in practice.

9. Giant Molecules

Chains of Atoms

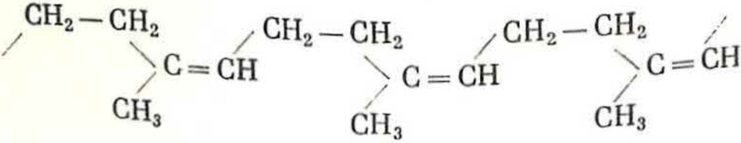
Chemists and technologists have been dealing for a long time with natural substances consisting of long molecules in which the atoms are bound like the links of a chain. We find examples on every hand: abundant substances as rubber, cellulose and protein constitute chain-type molecules made up of many thousands of atoms. The structural conceptions of such molecules were formed and developed in the twenties, when chemists learned to produce such substances in their laboratories.

One of the first steps in producing substances built of long-chain molecules was the creation of synthetic caoutchouc. This brilliant research was completed in 1926 by the Soviet chemist Sergei Vasilyevich Lebedev (1874-1934). The industrial production of synthetic caoutchouc (as crude rubber is called) was a vital problem in the USSR as it was in great demand for the manufacture of automobile tires (rubber is made of caoutchouc, or crude rubber) and because the rubber tree requires a tropical climate for its cultivation.

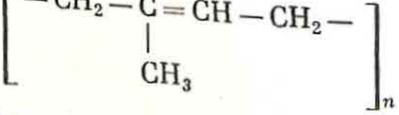
The hevea, or simply rubber, tree flourishes in the Brazilian jungle and from it oozes latex, a milky liquid that is a suspension of crude rubber. The Brazilian Indians made balls of crude rubber and also used it for making footwear. But in 1839, Charles Goodyear (1800-1860) originated the process for vulcanizing crude rubber. Treating crude rubber with sulphur and subjecting it to heat convert the sticky plastic crude rubber into elastic rubber.

At first the demand for rubber was low, but today mankind requires millions of tons annually. As we have already mentioned, rubber trees grow only in tropical forests so that countries in cold or temperate zones must produce synthetic rubber in plants on an industrial scale to avoid dependence on crude rubber imports.

To produce synthetic crude rubber, it is necessary, of course, to know what crude rubber (caoutchouc) is. When Lebedev began his investigations, the chemical formula of crude rubber was already known. It has the following form:



The chain shown here has neither beginning nor end. We see that the molecules are built up of identical links. We can therefore write the formula for crude rubber in a more concise form:



$$\left[-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-\right]_n$$

The quantity n may reach many thousands. Long-chain molecules built of repeating groups are called *polymers*.

An enormous number of synthetic polymers have found most extensive application in engineering and in the textile industries. They include nylon, polyethylene, capron, polypropylene, polyvinyl chloride and many, many others.

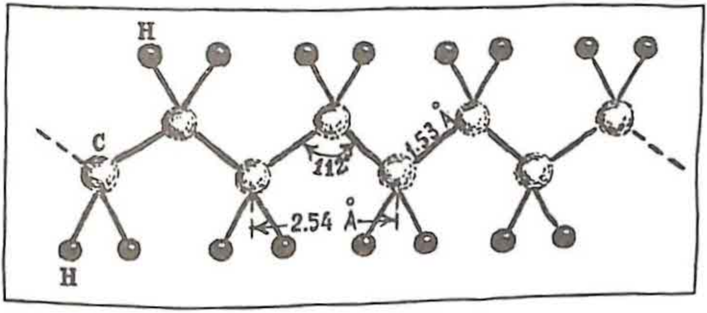


Figure 9.1

Of simplest structure are the molecules of polyethylene. Bags of this material are found in the kitchen tables of houses and apartments almost all over the world. If a molecule of polyethylene is stretched as far as it will go, it resembles the illustration in Figure 9.1. As you can see, physicists were able to determine the distances between the atoms and the angles between the valence bonds.

Long-chain molecules are not necessarily polymers, i.e. they do not necessarily consist of repeating groups. Chemists have learned to "design" molecules built up of two or more different groups. If the groups alternate in a definite order, for example, according to the arrangement ABABABABAB, it is still appropriate to call such a molecule a polymer. We often deal, however, with molecules not having such an ordered sequence. Can we call a molecule with the arrangement ABBBABABAAA-BBBBABABAABBA a polymer? This, however, is a matter of taste and tastes in names may differ.

A natural protein molecule is rarely called a polymer. Proteins are built up of some twenty pieces of different kinds. These pieces, or building blocks, are called amino acid radicals.

There is one essential difference between protein molecules and synthetic molecules built up of several pieces arranged in disorder. No two molecules are the same in a piece of synthetic polymer. Such a chain molecule may consist of one random sequence of component pieces, with another, different random sequence in another molecule. This usually has a detrimental effect on the properties of the polymer. If the molecules do not resemble one another, they cannot be efficiently packed together. In principle, such molecules cannot build up a crystal. Substances of this type produce amorphous glasses.

In the last decades, chemists have learned to build regular polymers, and have thus made many valuable materials available to industry.

As to natural proteins of a definite type (say the hemoglobin of a bull), the molecules are all the same even though they have a disordered structure. A molecule of protein of a given sort can be compared to a page of a book: the letters follow one another in a random, but quite definite order. All the molecules of a protein are copies of the same page of the book.

Flexibility of Molecules

A long-chain molecule can be likened to a rail. A line 0.1 mm long can accommodate a million atoms. The crosswise dimension of a molecule of polyethylene is about 3 or 4 Å. Thus the length of the molecule is greater than its width by several hundred thousand times. Since a rail of the kind used in railways has a thickness of about 10 cm, with the same length-to-thickness ratio as the molecule, the rail would have to be 10 km long.

This does not imply, of course, that there are no shorter polymer molecules. Unless special measures are taken, we find in a polymer substance molecules of different

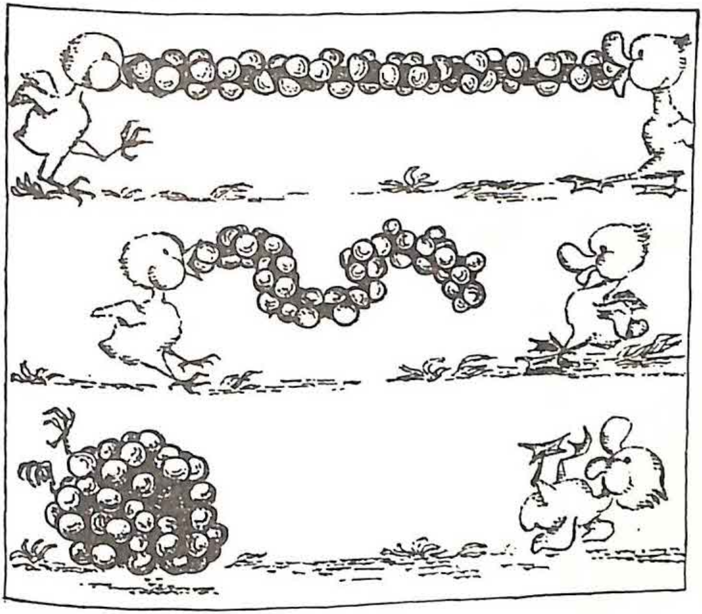


Figure 9.2

lengths, from one consisting of several groups to those built up of thousands of groups.

We likened a long-chain molecule to a rail. In another sense, this is not a very apt comparison. A rail is difficult to bend, while a molecule bends easily. The flexibility of a macromolecule is not similar to that of a willow switch. The molecule owes its flexibility to a capacity possessed by all molecules: one part of the molecule can swivel about another part if they are joined by bonds that chemists call single (monovalent) bonds. We can readily understand that this property of polymer molecules enables them to assume the queerest shapes. Illustrated in Figure 9.2 is a model of a flexible molecule in three positions. If a molecule is suspended in a solution, it is usually coiled into a ball.

The stretching of a rubber band consists in the uncoiling of its molecules. Thus, the flexibility of polymers is of an entirely different nature than that of metals. If the stretched band is released, it contracts to its former length. Hence, the molecule tends to go over from its linear (stretched) shape to a coiled one. Why does this occur? There are two possible reasons. In the first place, we can assume that the coiled shape is more advantageous from energy considerations. In the second place, we can suppose that coiling contributes to an increase in entropy. Hence, which law of thermodynamics governs this behaviour: the first or the second? Evidently, both. But the coiled state is doubtlessly advantageous from the entropy viewpoint as well. Obviously, the sequence of the atoms of molecules coiled into a ball is in more disorder than when the molecules are stretched out in a straight line. We also know that disorder and entropy are closely related.

Globular Crystals

Many molecules are capable of winding up into tight coils or, as they are sometimes called, globules. Very neat and quite identical globules make up a protein molecule. There is one subtle reason for this. As a matter of fact, a protein molecule contains parts that "like" water, and other parts that have an aversion to water. The parts that do not "like" water are said to be hydrophobic. The coiling of the protein molecules is governed by a single tendency: all the hydrophobic parts are to be hidden inside the globule. This is why the globules in a solution of protein resemble one another like identical twins.

Protein globules are more or less spherical. The size of a globule ranges from 100 to 300 Å, making it read-

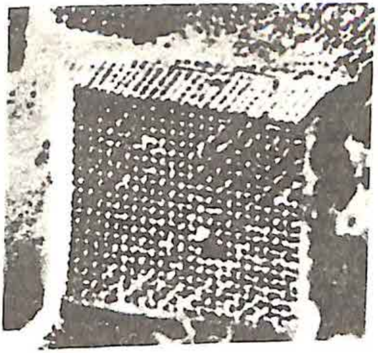


Figure 9.3

ily visible under an electron microscope. The first electron micrographs of globular crystals were obtained several decades ago, when electron microscopy techniques were considerably less advanced than they are today. Such a photograph of the tobacco mosaic virus is shown in Figure 9.3. A virus is more complex than a protein, but this example is quite suitable to illustrate our point, the tendency of biological globules to an exceptionally high degree of order.

But why haven't the authors provided a micrograph of a protein crystal? The answer is simple. Protein crystals are absolutely extraordinary. They contain an immense amount of water (sometimes up to 90%). This makes it impossible to photograph them in an electron microscope. Protein crystals can be investigated only by manipulating them in a solution. A tiny flask contains the solution and a monocrystal of the protein. This object can then be studied by all available physical methods, including X-ray structure analysis, which we have repeatedly mentioned.

Notwithstanding the huge amount of water—ordinary water, no different from tap water—the globular protein molecules are arranged in absolutely strict order. Their orientation to the axis of the crystal is the same for all the molecules. We have already mentioned that the molecules are identical. This superior order enables the structure of the protein molecule to be determined. This is no simple task and the investigators Max Ferdinand Perutz (b. 1914) and John Cowdery Kendrew (b. 1917), the first to determine the detailed structure of hemoglobin and myoglobin, were awarded a Nobel prize for their work.

The structure of about a hundred protein molecules is known today. Research continues in this field. Altogether, there are about ten thousand different proteins in a living organism. The activity of the living organism depends upon the way in which the proteins are coiled and in which order the different amino acid radicals follow one another in the molecule. No doubt that research concerning the structure of protein molecules will continue until all the details of the ten thousand kinds of molecules that govern life processes have been completely cleared up.

Bundles of Molecules

If molecules can be closely packed when they are stretched to the limit, the solid polymer material they comprise can form various quite complex structures that possess one common property. The solid body contains more or fewer regions in which the molecules adjoin one another like a bundle of pencils held in the fist.

Depending upon the percentage of such bundle-type regions in the body, and on how neatly the molecules comprising each such region are packed, the polymer possesses a certain "degree of crystallinity". Most polymers object to being simply classified as either amorphous or crystalline solids. There is nothing strange in this because we are dealing with giant molecules and, moreover, most-

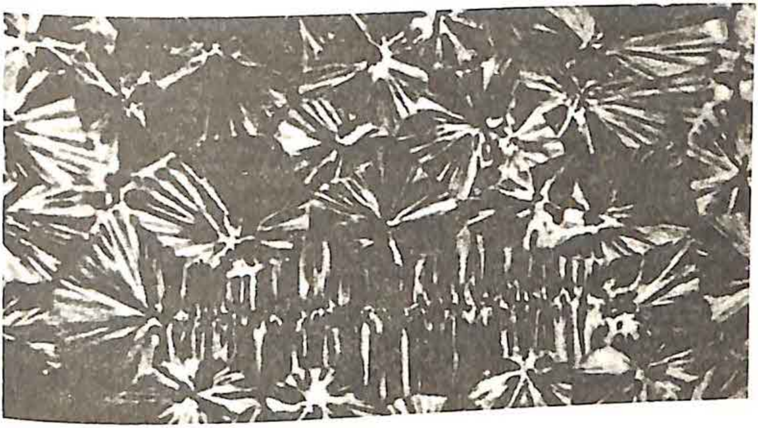


Figure 9.4

ly of different kinds. Ordered ("crystalline") regions in polymers can be roughly divided into three classes: bundles, spherulites and crystals of folding molecules.

A typical microstructure of a polymer is shown in Figure 9.4. This photograph has been magnified 400 times and was made from a film of polypropylene. The star-shaped figures are kinds of crystallites. The growth of the spherulite began from the centre of the star as the polymer was cooled. Then the spherulites met and interfered with one another's growth. Consequently, they did not acquire a perfect spherical shape (if you succeed in observing the growth of a separate spherulite, you will actually see a sphere, so that the name is justified). Inside the spherulite, the long molecules are arranged with sufficient neatness. Most likely, a spherulite can be envisioned as a neatly coiled rope. The rope represents a bundle of molecules. Thus the long axis of the molecules is positioned perpendicular to a radius of the spherulite. On the same

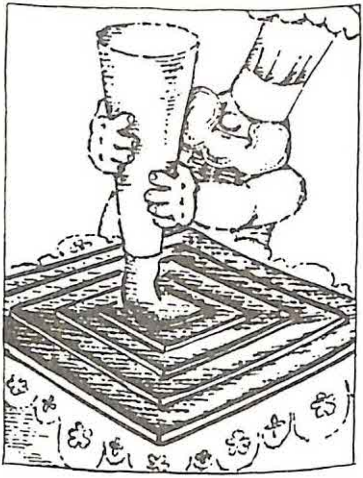


Figure 9.5

photograph we see lamellar regions. These may consist of bundles of molecules, or they may be crystals of folding molecules. The existence of such crystals is, perhaps, one of the most interesting and absolutely authentic facts concerning the structure of polymers.

The following outstanding discovery was made twenty years ago. Small crystals of various polymer substances were separated out of solutions. The investigators were astonished to find that the same kind of crystals, with a surface resembling a winding staircase, grew from solutions of various paraffins. What is the cause of spiral growth of crystals which look like they had been prepared by a skilled pastry-cook (Figure 9.5)?

When we discussed crystal growth on p. 119, we omitted one important circumstance. Imagine that a growing plane (face) of a crystal is completely filled with atoms. No positions remain that attract new atoms strongly enough. This being the case, it can be calculated that growth should proceed at an inconceivably slower rate

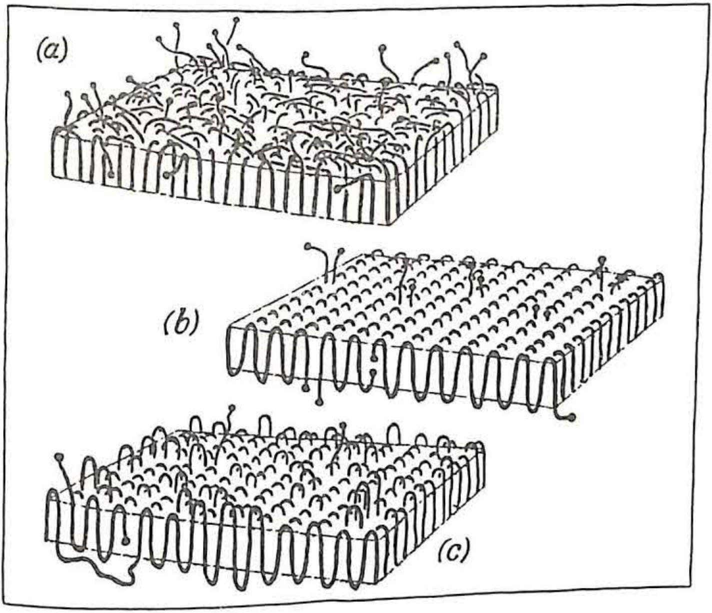


Figure 9.6

than that actually observed. This contradiction between theory and practice was finally solved: such rapid crystal growth was found possible when there are screw dislocations in the growing crystal. If there is a screw dislocation, the faces grow so that the steps at which new atoms can be readily attached never grow out to the edge of the crystal where they disappear. Physicists were certainly relieved when screw dislocations extricated them from their dilemma. The growth rates became clear as did the essence of the winding staircase feature indicated above for paraffin. Such spiral pyramids are frequently observed, and there is nothing strange about the fact that they exist.

Nothing strange while we are referring to crystals built up of small molecules. The explanation is appropriate for such crystals: the size of the molecules, height of the steps and the thickness of the crystal are all data that do not contradict one another.

But, when such a picture of crystal growth is observed in a polymer, it is, at first, puzzling. The point is that the thickness of the layers of polyester ranges from 100 to 120 Å, while the length of the molecule is 6000 Å. What conclusion can we reach on the basis of these figures? There is only one feasible explanation: the molecules are folded in these crystals. The flexibility of the molecules enables them to fold without difficulty. All that remains is to ponder (and such pondering continues to the present day) over the choice of the most suitable of the three models illustrated in Figure 9.6. The differences between the models are only minor ones. However, a specialist in this field will resent such a statement. "How can you call them minor?" he will object. "In the upper drawing, the molecules are folded over haphazardly, skipping their nearest neighbours; in the second model, the molecules become their own neighbours. The difference between the second and third models is that the surface of the crystal is smoother in the middle drawing than in the lower one."

The specialist is right: the packing or stacking arrangement of polymer molecules is of exceptional significance and has a fundamental effect on the properties of the substance. Although polyethylene, nylon and like materials were first synthesized several decades ago, the study of tneir supramolecular structure and investigation in the techniques required to pack the molecules in different ways are being continued to this day by many scientists in this field.

Muscular Contraction

We shall complete our discussion on giant molecules by considering an example that demonstrates how macromolecules behave in a living organism.

Biologists considered it to be their task to explain the conformity of the shapes of living organs—for instance, the shape of the hand or a leaf of a tree—to the functions of the organs.

Physicists, having decided to apply methods for investigating the structure of matter and the laws of nature in studying processes that occur in living organisms, are making efforts to understand life at the molecular level. The structure of tissues can be investigated today in great detail. After establishing the structure, it becomes feasible to develop a model of biological events.

A quite significant achievement in this line is the advancement of the theory of muscular contraction. The muscle fibre consists of two types of threads: thin ones and thick ones (Figure 9.7*a*). The thick threads consist of protein molecules called myosin. Physicists have established that a myosin molecule has the shape of a rod with a thickening at the end. In the thick thread, the molecules join with their thickened tails in the middle (Figure 9.7*c*). The thin threads consist of actin whose structure resembles two strings of beads forming a double helix. Muscle contraction consists in the thick threads sliding into the helixes of the thin threads.

The details of this mechanism are known, but we cannot discuss them here. The signal for a muscle contraction is given by a nerve pulse. Its arrival releases atoms of calcium which transfer from one part of the thread to another. As a result, the molecules turn towards one another so that it becomes advantageous from an energy viewpoint for one set of molecules to slide into the other set. The

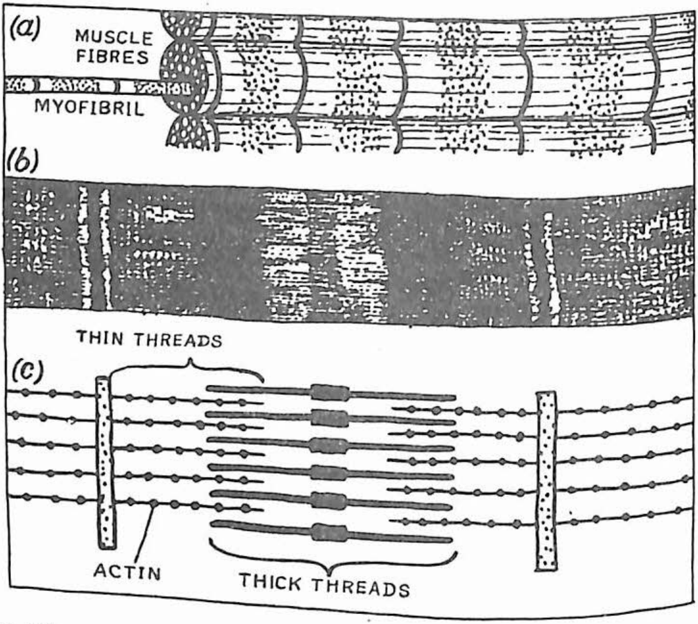


Figure 9.7

illustration gives two schematic diagrams with an electron photomicrograph (Figure 9.7*b*) between them.

I fear that these pages provide only a faint idea of the degree of detail to which the mechanism of muscle contraction has been studied. But our aim was only to interest the reader. Consider the last page of this book devoted to molecules as only a preview of a detailed discussion on biological physics which we hope to include in one of the subsequent books of *Physics for Everyone*.

To the Reader

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